Theory of anharmonically modified Coriolis coupling in the S_1 state of benzene and relation to experiment

Adam Helman and R. A. Marcus
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

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Avoided crossings between quasidegenerate rovibrational states in the Doppler-free two-photon excitation of the 14^1 mode in the S_1 excited state of benzene are treated theoretically. Two sets of avoided crossings in plots of spectral line frequency vs J at a given K and ΔK have been reported experimentally between an initially prepared "light" state (14^1 in zeroth order) and dark states, namely, one which in zeroth order is a $5^1 10^1 16^1$ state, the other being in zeroth order a $6^2 11^1$ and/or possibly a $3^1 16^1$ state, implicated earlier by Neusser *et al.* The identification of these states makes the phenomenon an excellent candidate for treatment of the avoided crossing via a Van Vleck transformation, no other basis set states being needed for the diagonalization in order to extract the important features. Two successive transformations are used for handling direct coupling and coupling via virtual states. The dominant calculated contribution to the coupling is, jointly, Coriolis plus cubic–cubic anharmonic interactions between vibrational modes. Playing less of a role are Coriolis terms in which the inverse moment of inertia tensor is expanded up to quadratic terms in the coordinates. There results a 5×5 (for coupling to $5^1 10^1 16^1$) and a 3×3 (for coupling to $6^2 11^1$ or $3^1 16^1$) matrix of the transformed Hamiltonian, each of which can also be described, if desired, to a very good approximation by a 2×2 matrix. The coupling element V_0 and the difference of the rotational constants for the light and dark states (ΔB) are obtained from the plots of line position vs $J(J+1)$ obtained. For the 14^1 to $5^1 10^1 16^1$ and for the 14^1 to $6^2 11^1$ couplings the theoretical results are in reasonable agreement with the experimental results, no adjustable parameters being employed. For a coupling of 14^1 to $3^1 16^1$ the calculated V_0 would be much too high compared with experiment (a factor of 10), the coupling involving the exchange of only three instead of four vibrational quanta. A situation in which the 14^1 state is coupled to the $6^2 11^1$ state to yield an avoided crossing and off-resonantly coupled to the $3^1 16^1$ state would be consistent with some experimental results and not affect the reasonable agreement of the slope difference and splitting for the avoided crossing plots.

I. INTRODUCTION

Recent advances in Doppler-free two-photon electronic spectroscopy have led to rotationally resolved electronic spectra of a molecule such as benzene.[1–9] It has been possible to excite in this way an exact single rovibronic quantum state and observe the results of avoided crossings with other eigenstates, avoided crossings which reflect couplings of the various zeroth-order states.

For a moderate size molecule such as benzene, many states may contribute to the intramolecular dynamics at high vibrational energies.[10–19] While we have used artificial intelligence search methods to select subsets of states for treating CH overtone spectra of benzene at higher energies,[20,21] they are not needed for the present relatively low energy study at 1570 cm^{-1}.

The current work is an extension of earlier work[20,21] in this laboratory, by incorporating rotational degrees of freedom, and was motivated by the highly interesting experimental results of Riedle, Neusser, Schlag, and co-workers.[1–9] In studies of Doppler-free two-photon spectroscopy, involving the preparation of single rovibronic states in the S_1 excited state of benzene, the authors reported a fit of 90% of their lines to a Hamiltonian based upon the RRHO (rigid rotor harmonic oscillator model), plus inclusion of lowest order Coriolis corrections.[5,6] Among the remaining absorption spectral lines there were displacements of the lines from their expected positions, some displacements, at least, being due to avoided crossings in plots of line position vs J at a given K and ΔK. They are considered here.

In the present paper the relevant data are considered for an initially prepared vibrational state of S_1 benzene, which is dominantly 14^1 in zeroth order,[22] and the experimental results are analyzed theoretically. Since the excess vibrational energy for the 14^1 state is only 1570 cm^{-1}, the possibility of only a few "final" dark states being implicated in causing the spectral perturbations is a real one.[7] In Sec. II A the Hamiltonian for the higher order vibration–rotation interactions relevant to the 14^1 state are given. Group theory and degeneracy in the vibrational states play an important role here in treating the experimental data. In Sec. II B the selection of dark states is considered. Section II C contains the contact transformation formalism required for the present treatment. In Secs. II D to II G we consider the matrix formulation for the coupling of the 14^1 "light" state with various zeroth-order "dark" states, each coupling having unique

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features warranting a separate discussion. In Sec. III results are given specifically for the dominantly 14^1 light state, and assignments are included of specific lines perturbed by interaction of the 14^1 zeroth-order state, separately, with the dark zeroth-order states $5^1 10^1 16^1$, $6^2 11^1$, and $3^1 16^1$, and jointly with $6^2 11^1$ and $3^1 16^1$.[7] In Sec. IV the dependence of the present theoretical coupling constants of these states upon the anharmonic force field is described. The results are given for differences of slopes in avoided crossings when plotted vs $J(J+1)$, rather than vs J, and for the splittings at the avoided crossings. Implications are summarized in Sec. V.

In the present paper we focus on a detailed approach which involves no adjustable parameters. We should mention another approach, an analytical one, which has been used at higher energy (3412 cm^{-1}) for the $14^1 1^2$ state of S_1 benzene.[23] The authors employed a model in which there was assumed an equidistant spacing of zeroth-order dark states coupled to the $14^1 1^2$ light state, a single value for a Coriolis coupling parameter and one for a cubic anharmonic parameter. The formalism was used to treat the linewidths of the given $S_0 \rightarrow S_1$ band.

II. THEORY

A. Hamiltonian

The eigenvalues of vibrating–rotating molecules have been extensively treated theoretically. One well-known method involves a perturbative expansion of the molecular Hamiltonian, with terms arranged according to the number of vibrational and rotational operators:[24–29]

$$\mathbf{H} = \sum_m \sum_n \lambda^{m+n-2} \mathbf{H}_{mn}, \tag{2.1}$$

where λ is a perturbation parameter, and m and n denote the degree of vibrational and rotational operators, respectively. $\mathbf{H}_{20}$ corresponds to the harmonic oscillator (HO) Hamiltonian, and $\mathbf{H}_{02}$ to the rigid rotor (RR) one. The lowest order term containing Coriolis coupling is $\mathbf{H}_{21}$, and involves two normal modes Q_k and Q_l, whose representation for their symmetric direct product contains the irreducible representation $\Gamma(R_\alpha)$ of a rotation about an axis α.[30]

The rovibrational energy of an oblate symmetric top, such as benzene, is given using RRHO and first-order Coriolis terms by

$$E = E_{\text{vib}} + B_e J(J+1) + (C_e - B_e)K^2 - 2C_e \times \left(\sum_i \zeta_i l_i\right) K, \tag{2.2}$$

where E_{vib} denotes the rotationless vibrational origin and the sum is over the degenerate vibrational modes which possess vibrational angular momenta $l_i \hbar$, about a sixfold symmetry axis in the case of benzene. The total rotational quantum number is J, K is that of the body-fixed component of the angular momentum along the sixfold symmetry axis, and C_e is the rotational constant (equilibrium configuration) for rotation about this axis.[31] B_e is the corresponding constant for rotation about one of the other symmetry axes. For a planar symmetric top such as benzene, $C_e = B_e/2$.

Although Eq. (2.2) sufficed to give the line positions in about 90% of cases,[5,6] explaining the remaining set of perturbed line positions requires a systematic investigation of operators in a more complete vibration–rotation Hamiltonian. In the latter one may expand the vibrational potential energy as a polynomial in normal coordinates, with the kinetic energy having only terms quadratic in their conjugate momenta. However, curvilinear coordinates have the advantage of realistically describing the atomic motions in terms of bond stretches, angle bends, etc., with the disadvantage of a $\mathbf{G}$ matrix[32] that is a function of the coordinates, yielding an expansion that results in higher-order terms in the kinetic energy operators.[33] Since the quadratic force field employed is expressed in terms of normal coordinates,[34] and since the resulting formulation of Coriolis operators is simpler, it is convenient in the present case to use normal coordinates in our expansion. Since the anharmonic force field employed[35] is expanded in curvilinear coordinates, the nonlinear transformation of force constants from curvilinear to normal coordinates would usually be required.[33] This transformation leaves the quadratic force field unaltered, would introduce correction terms converting the curvilinear quadratic force constants partly into the Cartesian cubic constants (expressed in normal coordinates), and introduces quadratic and cubic curvilinear force constant terms in the quartic constants expressed in Cartesian normal coordinates. However, the quadratic force field employed is a best fit to the experimental frequencies, and hence implicitly has accounted for the correction terms which would otherwise have to be applied. The anharmonic cubic Cartesian constants are then identical with the cubic curvilinear anharmonic constants, and are used here.

The various terms $\mathbf{H}_{mn}$ in Eq. (2.1) include those arising from expansion of the inverse inertia tensor μ which appears in the quantum-mechanical vibration–rotation Hamiltonian $\mathbf{H}$[36]:

$$\mathbf{H} = \frac{1}{2} \sum_{\alpha,\beta} \mu_{\alpha\beta} (\mathbf{J}_\alpha - \mathbf{p}_\alpha)(\mathbf{J}_\beta - \mathbf{p}_\beta) + \frac{1}{2} \sum_k \mathbf{P}_k^2 + V(\mathbf{Q}) - \frac{1}{8} \hbar^2 \sum_\alpha \mu_{\alpha\alpha}. \tag{2.3}$$

$\mathbf{J}_\alpha$ is a body-fixed component of the total angular momentum operator $\mathbf{J}$, with $\alpha = x,y,z$. $\mathbf{p}_\alpha$ is the αth component of the vibrational angular momentum operator

$$\mathbf{p}_\alpha = \sum_{k,\sigma_k,l,\sigma_l} \zeta^{(\alpha)}_{k,\sigma_k,l,\sigma_l} \mathbf{Q}_{k,\sigma_k} \mathbf{P}_{l,\sigma_l}, \tag{2.4}$$

where one cannot have, simultaneously, $k = l$ and $\sigma_k = \sigma_l$. In Eq. (2.4) $\mathbf{Q}_{k,\sigma_k}$ is the operator for the (mass weighted) normal mode (k,σ_k), while $\mathbf{P}_{l,\sigma_l}$ is the operator for the momentum conjugate to $\mathbf{Q}_{l,\sigma_l}$, and $\zeta^{(\alpha)}_{k,\sigma_k,l,\sigma_l}$ is a coefficient whose magnitude does not exceed unity.[37] The σ subscripts label components of degenerate modes and are absent for nondegenerate modes. The second and third terms on the right-hand side are, respectively, kinetic and potential normal mode energies, plus anharmonic terms in V.

In its equilibrium nuclear configuration the molecule has a principal axis system in which the inertia tensor is diagonal, $\mu^{(0)}_{\alpha\beta} = \delta_{\alpha,\beta} \mu^{(0)}_{\alpha\alpha}$. The rigid rotor (RR) approxima-

tion is recovered using $\mu_{\alpha\alpha}^{(0)}$ and neglecting vibrational angular momenta and vibrational anharmonicities. The lowest order Coriolis interaction $\mathbf{H}_{21}$ arises from the cross terms in $\mathbf{J}$ and $\mathbf{p}$, upon substitution of $\mu_{\alpha\alpha}^{(0)}$ for $\mu_{\alpha\beta}$. As in Eq. (2.4), it is a sum of terms each of which contains two vibrational operators and one rotational operator.

Aside from $\mathbf{H}_{21}$ there are terms $\mathbf{H}_{m1}$, $m \geqslant 3$, arising from expansion of $\mu_{\alpha\beta}$ in Eq. (2.3) in normal mode coordinates. The $\mathbf{H}_{m1}$ terms contain m vibrational operators and one rotational operator. In particular, the first two terms are

$$\mathbf{H}_{31} = -\frac{1}{2}\sum_{\alpha,\beta}\sum_{a,\sigma_a}\left[I_{\alpha\alpha}^{(e)}I_{\beta\beta}^{(e)}\right]^{-1}\Omega_{a,\sigma_a}^{(1)\alpha\beta}(\mathbf{p}_\alpha \mathbf{Q}_{a,\sigma_a} + \mathbf{Q}_{a,\sigma_a}\mathbf{p}_\alpha)\mathbf{J}_\beta, \tag{2.5}$$

$$\mathbf{H}_{41} = -\frac{1}{2}\sum_{\alpha,\beta}\sum_{a,\sigma_a b,\sigma_b}\left[I_{\alpha\alpha}^{(e)}I_{\beta\beta}^{(e)}\right]^{-1}\Omega_{a,\sigma_a b,\sigma_b}^{(2)\alpha\beta} \times(\mathbf{p}_\alpha \mathbf{Q}_{a,\sigma_a}\mathbf{Q}_{b,\sigma_b} + \mathbf{Q}_{a,\sigma_a}\mathbf{Q}_{b,\sigma_b}\mathbf{p}_\alpha)\mathbf{J}_\beta, \tag{2.6}$$

where
$\Omega_{a,\sigma_a}^{(1)\alpha\beta}, \Omega_{a,\sigma_a b,\sigma_b}^{(2)\alpha\beta}$, etc., are coefficients in the expansion of $\mu_{\alpha\beta}$:

$$\mu_{\alpha\beta} = \left[I_{\alpha\alpha}^{(e)}I_{\beta\beta}^{(e)}\right]^{-1}\left[I_{\alpha\beta}^{(e)} + \sum_{b,\sigma_b}\Omega_{b,\sigma_b}^{(1)\alpha\beta}Q_{b,\sigma_b} + \sum_{b,\sigma_b}\sum_{c,\sigma_c}\Omega_{b,\sigma_b c,\sigma_c}^{(2)\alpha\beta}Q_{b,\sigma_b}Q_{c,\sigma_c} + \cdots\right]. \tag{2.7}$$

The coordinates Q are defined so that they vanish at the equilibrium geometry. $\mathbf{H}_{31}$ and $\mathbf{H}_{41}$ are seen to reflect a vibrational dependence of the Coriolis term.

To proceed further we require the combination or other bands which may anharmonically and/or Coriolis-couple, near resonantly, to the 14^1 state. Identifying them is a step in deciding which terms in the vibration–rotation Hamiltonian are responsible for the coupling of 14^1 to dark states, i.e., to states whose Franck–Condon factors for their optical excitation from the ground state are very small.

B. Selection of dark states

Using only the experimental fundamental frequencies[34] ν_i in the S_1 state of benzene, it was possible to calculate combination band origins with an accuracy of perhaps ± 5 cm^{-1}; the combination band origin having an energy slightly different from the simple sum of fundamental frequencies,[38] because of extra anharmonic contributions. This figure of ± 5 cm^{-1} is based upon comparison with calculated theoretical fundamental and combination band energies using the *ab initio* anharmonic force field employed.[35] The vibrational combination states within ± 25 cm^{-1} of the initial state (using measured fundamentals of S_1) were examined as possible candidates as the interacting dark states.

The initially prepared vibrational state 14^1 (more precisely, an eigenstate which is dominantly 14^1) lies 1570 cm^{-1} above the lowest vibrational state of S_1 benzene. A direct count of vibrational states lying within ± 25 cm^{-1} of 14^1 using the fundamentals for S_1 given by Robey and Schlag[34] reveals seven states of the correct parity (ungerade), each having some degeneracy in zeroth order. (14^1 is ungerade, such that states of gerade parity cannot nonradiatively couple to it.) Of these seven vibrational states, four states ($10^1 11^1 16^2$, $4^2 10^1 16^1$, $4^1 16^2 17^1$, and $4^1 16^5$) differ from 14^1 by five, six, or seven vibrational quanta. The remaining two, $5^1 10^1 16^1$ and $6^2 11^1$, differ by four quanta from 14^1 and were proposed earlier by Neusser and co-workers[5–9] as the dark states.

A recent double resonance study[39] by Page *et al.* yields a set of S_1 fundamental frequencies which, among other changes,[40] differs from the set of Robey and Schlag[34] in the value of ν_3. When this new value is employed in the direct count, the $3^1 16^1$ state, of ungerade parity, falls within ± 25 cm^{-1} of 14^1.

Since each successive power in λ of the vibrational–rotational Hamiltonian is accompanied by an additional vibrational or rotational operator [cf. Eq. (2.1)], a given operator coupling, say, $10^1 11^1 16^2$ to 14^1 will occur with one power of λ higher than the analogous operator coupling $5^1 10^1 16^1$ and $6^2 11^1$ to 14^1. In the present study terms in $\mathbf{H}$ up to and including λ^3, the lowest order possible for the allowed coupling of these states, are considered. Since the coupling terms of order λ^4 and higher are neglected, the four states above differing in five or more vibrational quanta from 14^1 are not considered further. For direct coupling of 14^1 to $3^1 16^1$ only terms up to and including λ^2 need consideration.

In the $5^1 10^1 16^1$ state the three excited vibrational modes are each out of plane; modes 10 and 16 are doubly degenerate and of e_{1g} and e_{2u} symmetry, respectively.[32] The $6^2 11^1$ vibrational state has a doubly excited in-plane mode 6 of e_{2g} symmetry and a singly excited out-of-plane mode 11, of a_{2u} symmetry.[32] In the $3^1 16^1$ state mode 3 is in-plane with a_{2g} symmetry.[32] Mode 14 is an in-plane mode of b_{2u} symmetry.[32]

Having identified potential dark states quasidegenerate with 14^1, we consider later which terms in the vibrational–rotational Hamiltonian may couple 14^1 to these dark vibrational states. Some terms may shift rovibrational states in the 14^1 manifold from their anticipated positions in the RRHO approximation, without coupling to rovibrational states in the $5^1 10^1 16^1$ and $6^2 11^1$ manifolds, and are not considered further. All calculations of the splittings and difference of slopes in the avoided crossing curves can be made modulo such shifts.

C. Contact transformation theory and application

In the present case, where the zeroth-order states have been identified, the contact transformation method is particularly useful to treat the coupling and is employed here.[41–43] It focuses on the perturbation of a cluster of states. It was introduced by Van Vleck and applied extensively by Nielsen and others to molecular vibrational–rotational interactions.[42,44–47] By using it, no other basis states need be considered in the present case, when the transformed Hamiltonian is employed in the diagonalization, and the relevant expressions are available in the text by Amat *et al.*[48] A recent survey of perturbative and other methods, including the contact transformation, is given by Sibert.[49] A projection operator formalism for the contact transformation is described by

several authors,[50,51] and its relation to the work of Nielsen *et al.* is discussed by Jorgensen *et al.*[52]

In the contact transformation method, as applied to a polynomial Hamiltonian [cf. Eq. (2.1)], successive unitary transformations are introduced, the first such that the terms in the new Hamiltonian up to and including order λ (arising from cubic anharmonicity, Coriolis interaction, etc.) commute with the RRHO Hamiltonian $\mathbf{H}_0$, which is of order λ^0. Thereby, the matrix elements of this new Hamiltonian obtained with the RRHO basis set are diagonal to order λ. A second contact transformation is then introduced to yield a new Hamiltonian whose terms up to and including terms in λ^2 have only diagonal matrix elements in the RRHO basis set, and so again commute with $\mathbf{H}_0$. At this point, in the present case, the terms of order λ^3 with four vibrational operators and one rotational operator [cf. Eq. (2.1)], arising from the transformations, are now the leading contributions to the off-diagonal elements of the transformed Hamiltonian. They provide the desired resonant couplings between the rovibrational states in 14^1 with the identified dark states, which differ from 14^1 in four vibrational quanta.[53] The resulting matrix is then diagonalized in the present case to avoid the small denominators (resonant terms) problem. There is one qualification to the above: The unitary transformation typically used in the literature, and also used here, does not diagonalize to order λ^2 the terms having l quantum numbers for doubly degenerate vibrations. Accordingly, they will contribute later, to order λ^2, to the off-diagonal terms. A similar remark applies to rotational terms containing the quantum number K.[54] Later, in treating quasidegenerate states which differ in four quanta simultaneously with those which differ in three, care must be taken in choosing the transformation, so as to avoid small denominators. We first review briefly the Van Vleck transformation, using the projection operator version, because of its transparency.

In the contact transformation method, a unitary transformation $\mathbf{H}^{(1)} = \mathbf{U}_1 \mathbf{H} \mathbf{U}_1^\dagger$ is applied, such that the off-diagonal matrix elements of the transformed Hamiltonian $\mathbf{H}^{(1)}$ are zero up to order λ, in the representation $|i\rangle$ which diagonalizes the unperturbed Hamiltonian $\mathbf{H}_0$. For this purpose, one sets $\mathbf{U}_1 = \exp\{i\lambda \mathbf{S}_1\}$ with the transformation function $\mathbf{S}_1$, then satisfying Eq. (2.8)[47]:

$$\mathbf{H}_1^{(1)} = \mathbf{H}_1 + i[\mathbf{S}_1, \mathbf{H}_0], \tag{2.8}$$

$\mathbf{H}_1^{(1)}$ is the term of order λ in the transformed Hamiltonian $\mathbf{H}^{(1)}$ and $\mathbf{S}_1$ is chosen so that $\mathbf{H}_1^{(1)}$ is diagonal in the basis set which diagonalizes $\mathbf{H}_0$. The diagonal elements of $\mathbf{H}_1^{(1)}$ equal those of $\mathbf{H}_1$ in this basis set [Eq. (2.8)].

These results can be written compactly in terms of a projection operator formalism: We use $\mathbf{P}_0$ to denote an operator which projects onto the subspace of the initial state or states (in the present case this subspace consists only of the $|14^1; J, K\rangle$ state and the quasidegenerate specified dark states), and $\mathbf{Q}_0$ is the operator which projects onto the complementary subspace of the remaining eigenvectors of $\mathbf{H}_0$. For brevity of illustration in this section and in Appendix A, but not in the actual calculations, the $\mathbf{P}_0$ subspace is treated as degenerate, with eigenvalue E_0. The more general treatment is given in Ref. 50. The above conditions placed on $\mathbf{H}_1^{(1)}$ above can be written in terms of $\mathbf{P}_0$ and $\mathbf{Q}_0$ as

$$\mathbf{P}_0 \mathbf{H}_1^{(1)} \mathbf{Q}_0 = \mathbf{Q}_0 \mathbf{H}_1^{(1)} \mathbf{P}_0 = 0 \tag{2.9}$$

and

$$\mathbf{P}_0 \mathbf{H}_1^{(1)} \mathbf{P}_0 = \mathbf{P}_0 \mathbf{H}_1 \mathbf{P}_0, \quad \mathbf{Q}_0 \mathbf{H}_1^{(1)} \mathbf{Q}_0 = \mathbf{Q}_0 \mathbf{H}_1 \mathbf{Q}_0, \tag{2.10}$$

all of which can be rewritten as

$$\mathbf{H}_1^{(1)} = \mathbf{P}_0 \mathbf{H}_1 \mathbf{P}_0 + \mathbf{Q}_0 \mathbf{H}_1 \mathbf{Q}_0. \tag{2.11}$$

The solution of Eq. (2.8) and Eq. (2.11) for $\mathbf{S}_1$ is given by[50] (Appendix A)

$$\mathbf{S}_1 = i \frac{\mathbf{Q}_0}{E_0 - \mathbf{H}_0} \mathbf{H}_1 \mathbf{P}_0 + \text{h.c.}, \tag{2.12}$$

where h.c. denotes the Hermitian conjugate, $-i\mathbf{P}_0 \mathbf{H}_1 \mathbf{Q}_0 / (E_0 - \mathbf{H}_0)$ in this case.

In the use of Eq. (2.12) for $\mathbf{S}_1$, each perturbing term $\mathbf{H}_{1;p}$ in the untransformed perturbation Hamiltonian ($\mathbf{H}_1 = \Sigma_p \mathbf{H}_{1;p}$) is seen to require a corresponding function $\mathbf{S}_{1;p}$, with $\mathbf{S}_1 = \Sigma_p \mathbf{S}_{1;p}$. For transformation functions relating different vibration–rotation terms in the Hamiltonian $\mathbf{S}_{1;p} = \mathbf{S}_{1;p}^{\text{vib}} \mathbf{S}_{1;p}^{\text{rot}}$. The zeroth-order RRHO Hamiltonian $\mathbf{H}_0$ equals $\mathbf{H}_{20} + \mathbf{H}_{02}$. Equation (2.12) then yields

$$i[\mathbf{S}_{1;p}, \mathbf{H}_0] = i[\mathbf{S}_{1;p}^{\text{vib}}, \mathbf{H}_{20}] \mathbf{S}_{1;p}^{\text{rot}} + i[\mathbf{S}_{1;p}^{\text{rot}}, \mathbf{H}_{02}] \mathbf{S}_{1;p}^{\text{vib}}, \tag{2.13}$$

since $\mathbf{S}_{1;p}^{\text{vib}}$ commutes with $\mathbf{H}_{02}$ and $\mathbf{S}_{1;p}^{\text{rot}}$ commutes with $\mathbf{H}_{20}$.[55]

The lowest order operator that will provide an off-diagonal coupling of the initial state with states which differ in four vibrational quanta and in K is the third-order twice-transformed operator $\mathbf{H}_3^{(2)}$. For this reason the Hamiltonian $\mathbf{H}^{(1)}$ is subjected to a second transformation, to make the off-diagonal matrix elements arising from perturbations to order λ^2 vanish, and the diagonal elements of $\mathbf{H}_2^{(2)}$ to equal those of $\mathbf{H}_2^{(1)}$, thereby isolating $\mathbf{H}_3^{(2)}$ as the leading term responsible for the coupling in the transformed Hamiltonian. However, as noted earlier, the standard Nielsen-type transformation functions $\mathbf{S}_1$ and $\mathbf{S}_2$ employed in the calculations allow for a matrix representation diagonal in the principal vibrational quantum numbers v_i to order λ^2, but *not* diagonal to order λ^2 with respect to the l_i quantum numbers in the case of doubly degenerate vibrations, nor with respect to the rotational quantum number K.[53,54]

The second contact transformation $\mathbf{S}_2$ will be sufficient for removing from the off-diagonal positions all terms of order λ^2, except for those off-diagonal in the l_i quantum numbers, in K, or in both. For the second transformation we have $\mathbf{H}^{(2)} = \mathbf{U}_2 \mathbf{H}^{(1)} \mathbf{U}_2^\dagger$, where $\mathbf{U}_2 = \exp\{i\lambda^2 \mathbf{S}_2\}$ and hence,

$$\mathbf{H}_2^{(2)} = \mathbf{H}_2^{(1)} + i[\mathbf{S}_2, \mathbf{H}_0], \tag{2.14}$$

where $\mathbf{H}_2^{(1)}$ is the term of order λ^2 in $\mathbf{H}^{(1)}$, i.e., in $\exp\{i\lambda \mathbf{S}_1\} \mathbf{H} \exp\{-i\lambda \mathbf{S}_1\}$:

$$\mathbf{H}_2^{(1)} = \mathbf{H}_2 + i[\mathbf{S}_1, \mathbf{H}_1] - \tfrac{1}{2}[\mathbf{S}_1, [\mathbf{S}_1, \mathbf{H}_0]]. \tag{2.15}$$

Analogously to Eqs. (2.9) and (2.10) we wish

$$\mathbf{P}_0 \mathbf{H}_2^{(2)} \mathbf{Q}_0 = \mathbf{Q}_0 \mathbf{H}_2^{(2)} \mathbf{P}_0 = 0 \tag{2.16}$$

and

$$\mathbf{P}_0\mathbf{H}_2^{(2)}\mathbf{P}_0 = \mathbf{P}_0\mathbf{H}_2^{(1)}\mathbf{P}_0, \quad \mathbf{Q}_0\mathbf{H}_2^{(2)}\mathbf{Q}_0 = \mathbf{Q}_0\mathbf{H}_2^{(1)}\mathbf{Q}_0, \tag{2.17}$$

and so we have

$$\mathbf{H}_2^{(2)} = \mathbf{P}_0\mathbf{H}_2^{(1)}\mathbf{P}_0 + \mathbf{Q}_0\mathbf{H}_2^{(1)}\mathbf{Q}_0. \tag{2.18}$$

The solution of Eqs. (2.14) and (2.18) is similar to that of Eq. (2.12):

$$\mathbf{S}_2 = i\frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{H}_2^{(1)}\mathbf{P}_0 + \text{h.c.}, \tag{2.19}$$

hence one finds from Eqs. (2.12) and (2.15) that

$$\mathbf{S}_2 = i\left[\frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{H}_2\mathbf{P}_0 + \frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{H}_1\frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{H}_1\mathbf{P}_0 - \frac{\mathbf{Q}_0}{\mathbf{a}^2}\mathbf{H}_1\mathbf{P}_0\mathbf{H}_1\mathbf{P}_0\right] + \text{h.c.}, \tag{2.20}$$

where $\mathbf{a} = E_0 - \mathbf{H}_0$.

The $\mathbf{S}_1$ and $\mathbf{S}_2$ transformation functions obtained by Nielsen and co-workers,[23-24,44,47] and the $\mathbf{S}_1$ and $\mathbf{S}_2$ functions discussed above using the projection operator formalism, satisfy the same equations, namely, Eqs. (2.8) and (2.14). Furthermore, $\mathbf{S}_1$ and $\mathbf{S}_2$ can be determined from those equations, e.g., as in Eqs. (2.12) and (2.19). However, Nielsen's and the projection operator forms of the **S** functions are quite different; the former being expressed in terms of polynomials of vibrational operators $\mathbf{q}_i$ and $\mathbf{p}_i$,[56] and the latter being expressed instead in terms of $\mathbf{P}_0$, $\mathbf{Q}_0$, and **H**. Nevertheless, they lead in the present case to the same final results for the transformed Hamiltonian when **H** is expressed in polynomial form. Thereby, it was appropriate to describe the overall formalism here using the projection operator expressions for **S** functions (they are simpler),[57] even though the transformed Hamiltonian used in the present calculations was that given in Ref. 48, where Nielsen **S** functions were used.

The term in $\mathbf{H}^{(2)}$ of present interest for coupling the 14^1 to the $5^110^116^1$ or 6^211^1 manifolds is $\mathbf{H}_3^{(2)}$ and is given by the term of order λ^3 in $\exp\{i\lambda^2\mathbf{S}_2\}\mathbf{H}^{(1)}\exp\{-i\lambda^2\mathbf{S}_2\}$, namely, by

$$\mathbf{H}_3^{(2)} = \mathbf{H}_3^{(1)} + i[\mathbf{S}_2,\mathbf{H}_1^{(1)}]. \tag{2.21}$$

Needed for the present problem, however, is not the full $\mathbf{H}_3^{(2)}$, but only its diagonal component, $\mathbf{P}_0\mathbf{H}_3^{(2)}\mathbf{P}_0$. Using Eqs. (2.10), (2.19), and (2.21) we have

$$\mathbf{P}_0\mathbf{H}_3^{(2)}\mathbf{P}_0 = \mathbf{P}_0(\mathbf{H}_3^{(1)} + i[\mathbf{S}_2,\mathbf{H}_1])\mathbf{P}_0. \tag{2.22}$$

Since $\mathbf{H}_3^{(1)}$ can be expressed in terms of $\mathbf{S}_1$, $\mathbf{S}_2$, and **H** alone, it follows from Eq. (2.22) that

$$\mathbf{P}_0\mathbf{H}_3^{(2)}\mathbf{P}_0 = \mathbf{P}_0\{\mathbf{H}_3 + i([\mathbf{S}_1,\mathbf{H}_2] + [\mathbf{S}_2,\mathbf{H}_1]) - \tfrac{i}{3}[\mathbf{S}_1,[\mathbf{S}_1,\mathbf{H}_1]]\}\mathbf{P}_0, \tag{2.23}$$

where $\mathbf{H}_2$ is the term of order λ^2 in **H**. Evaluation of the commutators in Eq. (2.23), using Eqs. (2.12) and (2.20), yields[50]

$$\mathbf{P}_0\mathbf{H}_3^{(2)}\mathbf{P}_0 = \mathbf{P}_0\left\{\mathbf{H}_3 + \mathbf{H}_1\frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{H}_2 + \mathbf{H}_2\frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{H}_1 + \mathbf{H}_1\frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{H}_1\frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{H}_1 - \frac{1}{2}\mathbf{H}_1\mathbf{P}_0\mathbf{H}_1\frac{\mathbf{Q}_0}{\mathbf{a}^2}\mathbf{H}_1 - \frac{1}{2}\mathbf{H}_1\frac{\mathbf{Q}_0}{\mathbf{a}^2}\mathbf{H}_1\mathbf{P}_0\mathbf{H}_1\right\}\mathbf{P}_0. \tag{2.24}$$

The terms in $\mathbf{P}_0\mathbf{H}_3^{(2)}\mathbf{P}_0$ in Eq. (2.24) contain the following matrix elements of products of untransformed operators, with $\mathbf{H}_{mn}$ again denoting m vibrational and n rotational operators: $\mathbf{H}_{41}$; $\mathbf{H}_{40}^{\text{quartic}}\mathbf{H}_{21}$, $\mathbf{H}_{40}^{\mathbf{P}_\alpha\mathbf{P}_\beta}\mathbf{H}_{21}$, $\mathbf{H}_{30}\mathbf{H}_{31}$; and $\mathbf{H}_{30}\mathbf{H}_{30}\mathbf{H}_{21}$ omitting for notational brevity the interspersed $\mathbf{P}_0$'s and $\mathbf{Q}_0$'s. Here, $\mathbf{H}_{40}^{\text{quartic}}$ arises from quartic anharmonicity and $\mathbf{H}_{40}^{\mathbf{P}_\alpha\mathbf{P}_\beta}$ from the cross terms of Eq. (2.3) quadratic in vibrational angular momenta. Each factor contributes its own order of λ, e.g., in the product $\mathbf{H}_{30}\mathbf{H}_{30}\mathbf{H}_{21}$, since $\mathbf{H}_{30}$ has a cubic anharmonicity, it is of order λ, the Coriolis factor $\mathbf{H}_{21}$ is of order λ, and so the terms are of order λ^3. Similarly, $\mathbf{H}_{40}^{\text{quartic}}\mathbf{H}_{21}$ and $\mathbf{H}_{40}^{\mathbf{P}_\alpha\mathbf{P}_\beta}\mathbf{H}_{21}$ are each of order λ^3.

The symmetry requirements for nonzero cubic and quartic force constants in $\mathbf{H}_{30}$ and $\mathbf{H}_{40}^{\text{quartic}}$ and for Coriolis coupling coefficients in $\mathbf{H}_{21}$ are well known.[32] The symmetry restrictions for the terms containing the $\Omega^{(1)\alpha\beta}_{Q_{a'}\sigma_a}$ and $\Omega^{(2)\alpha\beta}_{Q_{a'}\sigma_a Q_{b'}\sigma_b}$ coefficients were derived individually and are given in Appendix B. This information indicates which product operators vanish by symmetry when $\mathbf{H}_{31}$ and $\mathbf{H}_{41}$ appear singly in the products.

Upon performing the appropriate sums over the mode indices thousands of combinations of the vibrational operators are obtained for the various products above. Group theory was used to identify which of these products, via the relevant matrix elements, contribute to the coupling of the light and dark states (cf. Appendix B).

An important simplification in perturbation calculations of molecular rotation–vibration interactions, present in the formulas[48] used here, arises from (1) the algebraic simplification due to use of $[\mathbf{q}_i,\mathbf{p}_j]$ commutation relations, and (2) the simplicity of the matrix elements of $\mathbf{q}_i^2$, e.g., in Eq. (2.24). For example, for the second reason, in a coefficient $\Sigma_b\Sigma_c\, C_{bc}k_{abc}k_{cde}\zeta^{(a)}_{b,f}$ of a polynomial in the next section the operators $\mathbf{q}_b^2$ and $\mathbf{q}_c^2$ are absent in the polynomial.

D. Coupling of the 14^1 state to the $5^110^116^1$ manifold

The matrix elements coupling the zeroth-order 14^1 state and the zeroth-order dark state $5^110^116^1$ are considered as a specific example of the use of group theory in applying Eq. (2.24). For a term in a product operator $\mathbf{P}_0\mathbf{H}_3^{(2)}\mathbf{P}_0$ such as $\mathbf{H}_{30}\mathbf{H}_{30}\mathbf{H}_{21}$ to contribute to this coupling, each of the three factors must be nonzero. The expansion of the transformed

operator, $\mathbf{H}_{30}\mathbf{H}_{30}\mathbf{H}_{21}$ which couples $|i\rangle$ and $|j\rangle$, where $|i\rangle$ and $|j\rangle$ are in the $\mathbf{P}_0$ and $\mathbf{Q}_0$ subspaces, respectively, contains the matrix elements[58] $(\Sigma_b\Sigma_c C_{bc}k_{abc}k_{cde}\zeta^{\alpha}_{b,f})\langle i|\mathbf{q}_a\mathbf{q}_d\mathbf{q}_e\mathbf{p}_f\mathbf{J}_\alpha|j\rangle$ and $(\Sigma_a\Sigma_d C_{ad}k_{abc}k_{def}\zeta^{\alpha}_{a,d})\langle i|\mathbf{q}_b\mathbf{q}_c\mathbf{q}_e\mathbf{p}_c\mathbf{J}_\alpha|j\rangle$, where the indices which are not summed over depend on the dark state $|j\rangle$, for the given light state $|i\rangle$. In the first sum the representations $\Gamma(Q_a)\otimes\Gamma(Q_b)\otimes\Gamma(Q_c)$ and $\Gamma(Q_c)\otimes\Gamma(Q_d)\otimes\Gamma(Q_e)$ must each have an a_{1g} irreducible component, in order that k_{abc} and k_{cde} not vanish by symmetry, while $\Gamma(Q_b)\otimes\Gamma(Q_f)$ must have a $\Gamma(R_\alpha)$ component so that $\zeta^{\alpha}_{b,f}$ similarly does not vanish. These restrictions severely limit the allowed values of indices b and c, which would be otherwise free to vary. When the 14^1 and $5^110^116^1$ states are coupled, the indices a,d,e,f in the first sum become permutations of 5, 10, 14, and 16. The values of b and c for which the relevant matrix elements do not vanish can then be determined systematically using group theory (cf. Appendix B). In the above sums C_{bc} and C_{ad} are constants containing harmonic frequencies, moments of inertia, etc., and are seen to differ in which factors have the common indices. A discussion of the symmetry of terms in the first sum is given, as an illustrative example, in Appendix B.

For this pair of states only a small fraction, but still many, independent combinations of quadratic products of cubic constants multiplied by Coriolis coefficients contribute to the coupling. In the case of the other product operators, only a few terms are left. Later, in Sec. IV a breakdown of number of combinations and their relative contributions to the coupling matrix element of $\mathbf{H}_3^{(2)}$ are given. Here, rather, the few general types of nonzero combinations which arise are described. For this pair of states there is no contribution to the coupling from the first term in Eq. (2.23), $\mathbf{H}_3$, because of symmetry requirements for terms containing the $\Omega^{(2)\alpha\beta}_{Q_a\sigma_a Q_b\sigma_b}$ factors. This finding is evident from the result, seen in Appendix B, that for the identified initial and final states the four coupled vibrational quanta involved must have at least three of them in in-plane modes. However, for other initial-final pairs of states $\mathbf{H}_3$ could well contribute to the coupling.

We also have from $\langle i|\mathbf{H}_{40}^{\text{quartic}}\mathbf{H}_{21}|j\rangle$ the sum $\Sigma_a C_a\zeta^{\alpha}_{a,e}k_{abcd}\langle i|\mathbf{p}_e\mathbf{q}_b\mathbf{q}_c\mathbf{q}_d\mathbf{J}_\alpha|j\rangle$, which will be nonzero for some values of the index a. We further have[58] from $\langle i|\mathbf{H}_{30}\mathbf{H}_{31}|j\rangle$ the sum $\Sigma_c C_c\Omega_c^{(1)\alpha\beta}\zeta^{\alpha}_{d,e}k_{abc}\times\langle i|\mathbf{q}_a\mathbf{q}_b\mathbf{q}_d\mathbf{p}_e\mathbf{J}_\alpha|j\rangle$, which is similarly nonzero for some values of the index c, as again shown by symmetry arguments. Analogous results apply for coupling to the 6^211^1 final state[59] and to the 3^116^1 final state.

Now that coupling by many terms in the transformed Hamiltonian has been eliminated to order λ^2, the remaining couplings are considered for the present small set of rovibrational zeroth-order states in the initial and final manifolds.[60] In the example below, the $5^110^116^1$ state is considered. It has two doubly degenerate (e) modes, 10 and 16. The initial state is $|J,K\rangle$, with the vibrational excitation 14^1 understood, and the final state is $|J,K\pm1\rangle$, with the vibrational excitation specified later, there being two e- modes in the final state. The latter can be characterized, in part, by the additional quantum numbers l_{10} and l_{16} [these ls, which are zero in the initial state, are not associated with the vibrational angular momenta $l_i\hbar$ in Eq. (2.2), since modes 10 and 16 are each out of plane.] In the coupling of the 14^1 and $5^110^116^1$ states, J is conserved, and since the only type of Coriolis coupling allowed for the relevant states is (x,y) (for a z-Coriolis coupling to $5^110^116^1$ at least one of the modes in the dark state would have had to be in-plane) the selection rule for the radiationless transition is $\Delta K=\pm1$. This (x,y) Coriolis coupling, a consequence of the selected states and the symmetry requirements, is supported later by experiment.[7]

Due to symmetry present in a $\mathbf{C}_N$ operation about the principal symmetry axis the following selection rule applies for coupling between two zeroth-order states for a symmetric top[61]:

$$-\Delta K+\sum_t a_t\Delta l_t+\frac{1}{2}N\sum_i\Delta v_i=pN, \tag{2.25}$$

for a molecule with an N-fold principal symmetry axis (here, $N=6$). In Eq. (2.25) p is an integer, the sum over i is over all modes belonging to b-type irreducible representations (b_{1g}, b_{2g}, etc.,$\cdots$),[61] and the sum over t is over degenerate modes that change their respective l_t values by Δl_t, with a_t equal to one for an e_1-type mode (e_{1g},e_{1u}) and two for an e_2-type mode (e_{2g},e_{2u}). For a given ΔK, it provides the allowed Δl's.

In applying Eq. (2.25) to the coupling of 14^1 to the final state $5^110^116^1$ we note first that the latter state has an excited e_1-type mode Q_{10} (and hence $a_{10}=1$) and an excited e_2-type mode Q_{16} (and hence $a_{16}=2$). For $\Delta K=\pm1$, the smallest change in the l's is obtained by setting p and the Δv_i's in Eq. (2.25) equal to zero. Equation (2.25) now gives, for $\Delta l=\pm1$, corresponding to one vibrational quantum exchange per mode,

$$l_{10}=\pm1,$$
$$l_{16}=\mp1 \text{ simultaneously (for } \Delta K=\pm1). \tag{2.26}$$

Thereby, any Coriolis-induced $\Delta K=\pm1$ coupling between 14^1 and dark states with $l_{10}=l_{16}=\pm1$ is forbidden. These latter two states are therefore omitted from the set of basis states.

The successive transformations provide a matrix representation of the transformed Hamiltonian in which the initial and final states are in one 5×5 block along the main diagonal. Since the implicated coupling is of order λ^3 we do not include in this matrix any terms of higher order. Within this matrix given below there are also terms coupling the $K\pm1$ states to $K\pm2$ states, respectively. However, the $K\pm2$ states would be further off-resonance as seen by the rigid rotor energy term in $\mathbf{H}_0$, $B_e\left[J(J+1)-\frac{1}{2}(K\pm2)^2\right]$, having substituted $K\pm2$ for K, differing from the rigid rotor energy for K by about $\mp2B_eK\approx0.36K$ cm^{-1}. Thereby, such $K\pm2$ states can be omitted here in treating the properties of an avoided crossing. The remaining terms, being of order λ^0, λ^2, or λ^3 are included, the matrix elements being those of the indicated operators:

$\lvert l_{10}^{-}l_{16}^{+};J,K-1\rangle$	$\lvert l_{10}^{+}l_{16}^{-};J,K-1\rangle$	$\lvert 14^1;J,K\rangle$	$\lvert l_{10}^{-}l_{16}^{+};J,K+1\rangle$	$\lvert l_{10}^{+}l_{16}^{-};J,K+1\rangle$
$\mathbf{H}_0+\mathbf{H}_2^{(2)}$	$\mathbf{H}_2^{(2)}$	0	0	0
	$\mathbf{H}_0+\mathbf{H}_2^{(2)}$	$\mathbf{H}_3^{(2)}$	0	0
		$\mathbf{H}_0+\mathbf{H}_2^{(2)}$	$\mathbf{H}_3^{(2)}$	0
			$\mathbf{H}_0+\mathbf{H}_2^{(2)}$	$\mathbf{H}_2^{(2)}$
(Hermitian)				$\mathbf{H}_0+\mathbf{H}_2^{(2)}$

where only terms of the twice-transformed Hamiltonian for which the matrix elements are nonzero are shown.

In this matrix the states of $5^1 10^1 16^1$ parentage are labeled by quantum numbers l_{10} and l_{16}, the superscripts indicating their signs of ± 1. The initial zeroth-order state is indicated by $|14^1;J,K\rangle$, for which all l_i vanish, the Q_{14} mode being nondegenerate and all other modes being unexcited. The missing operators in the lower left triangle are the Hermitian conjugates of those listed in the upper right. The diagonal terms contain RRHO energies from $\mathbf{H}_0$, and the diagonal matrix elements for the two states of $5^1 10^1 16^1$ parentage with $J_z = K-1$ have the same RRHO values, as do the two states with $J_z = K+1$. There is no diagonal term linear in λ associated with parallel Coriolis energy or anharmonicity for this pair of states 14^1 and $5^1 10^1 16^1$,[37] and so there is no $\mathbf{H}_1^{(2)}$ term in this matrix. This latter statement follows because $\mathbf{H}_1^{(2)} = \mathbf{H}_1^{(1)}$ (since $\mathbf{S}_2$ has no effect on $\mathbf{H}_1^{(1)}$), and $\mathbf{H}_1^{(1)} = \mathbf{H}_1 = 0$, in the absence of parallel Coriolis contribution to the energy of these states and [cf. Eq. (2.11)] since $\mathbf{S}_1$ has no effect on diagonal elements of $\mathbf{H}_1$. There are diagonal terms of order λ^2, $\mathbf{H}_2^{(2)}$, some of which are dependent on vibrational quantum numbers alone, and others that are dependent on J and K. The former are included in ΔE_{vib}, the difference in energy of rotationless origins in the absence of l degeneracy, between $5^1 10^1 16^1$ and 14^1. The diagonal (J,K) dependent terms include quartic centrifugal distortion operators [such as $\mathbf{J}^2(\mathbf{J}+1)^2$] and terms proportional to $J(J+1)$ or K^2. Both give a negligible contribution to the energy difference of the two states and no contributions to the off- diagonal elements.[62]

Off-diagonal matrix elements are of the operators $\mathbf{H}_3^{(2)}$ and $\mathbf{H}_2^{(2)}$.[60] The third-order transformed operator $\mathbf{H}_3^{(2)}$ is seen to couple the initial K state to the final $K-1$ and $K+1$ states with the appropriate signs of l_{10} and l_{16} indicated. The operator $\mathbf{H}_2^{(2)}$, of order λ^2, removes the degeneracy of pairs of levels that differ only in their l quantum numbers, and via $\langle v_s,v_t;l_s \pm 1,l_t \mp 1|\mathbf{H}_2^{(2)}|v_s,v_t;l_s \mp 1,l_t \pm 1\rangle$ it provides the well-known l-type doubling.[63] The magnitude of this matrix element exceeds that of $\mathbf{H}_3^{(2)}$ and places one of this pair of levels off-resonance from the $|14^1;J,K\rangle$ state, thereby, allowing the latter to interact via $\mathbf{H}_3^{(2)}$ with the remaining state in the $5^1 10^1 16^1$ manifold.

The J's will be considered for which, prior to the diagonalization, the initial state 14^1 has a zeroth-order (RRHO) energy that is very close to the two states in the $5^1 10^1 16^1$ manifold with $J_z = K+1$. It can be seen[64] that, apart from changing the signs of the Δl_i's and modifying slightly the off-diagonal term, the use of $\Delta K = -1$ gives essentially the same final results. When the two $J_z = K+1$ dark states are quasidegenerate with the initial state $|J,K\rangle$ the two states with $J_z = K-1$ are relatively far removed in energy and one could introduce a partitioning approximation[65] in which the 2×2 subspace consisting of $|14^1;J,K\rangle$ and the nearest single nearby state with $J_z = K-1$ are regarded as forming the resonant subspace and the remaining three states as being off-resonant. The resulting secular equation yields the eigenvalues[66]

$$E_{1,2} = \frac{1}{2}\{(E_1' + E_2') \pm [(E_1' - E_2')^2 + 4|H_3^{(2)\prime}|^2]^{1/2}\}, \tag{2.27}$$

which yields immediately the deviations of the lines from their anticipated positions. In Eq. (2.27) $|H_3^{(2)\prime}|$ denotes the magnitude of the off-diagonal matrix elements due to the perturbation given by the transformed operator $\mathbf{H}_3^{(2)}$, plus additional terms arising from the partitioning method, while E_1' and E_2' are diagonal matrix elements of the two coupled states in this 2×2 matrix, thereby also containing off-resonant terms arising from the partitioning. Numerical results are given later, both with and without the partitioning approximation and indicate the usefulness of the latter.

E. Coupling of the 14^1 state to the $6^2 11^1$ manifold

For the dark states in $6^2 11^1$ there are now three states involved, the states $|14^1;J,K\rangle$, $|l_6^{-2};J,K-1\rangle$ and $|l_6^{+2};J,K+1\rangle$. There is one other difference from the preceding case of the $5^1 10^1 16^1$ states: there is now a first-order (parallel) Coriolis energy that appears on the main diagonal (mode 6 is a degenerate in-plane mode, and the Coriolis energy splits states differing in their l_6 quantum numbers). Since one of the two states $|l_6^{-2};J,K-1\rangle$, and $|l_6^{+2};J,K+1\rangle$ is well separated by the zeroth-order term in K^2 as well as by the first-order parallel Coriolis interaction from the remaining two states, that state is weakly coupled and the partitioning technique can again reduce the problem to a 2×2 secular equation, with a solution analogous to Eq. (2.27). The 3×3 matrix is given by

$\lvert l_6^{-2};J,K-1\rangle$	$\lvert 14^1;J,K\rangle$	$\lvert l_6^{+2};J,K+1\rangle$
$\mathbf{H}_0+\mathbf{H}_1+\mathbf{H}_2^{(2)}$	$\mathbf{H}_3^{(2)}$	0
	$\mathbf{H}_0+\mathbf{H}_2^{(2)}$	$\mathbf{H}_3^{(2)}$
(Hermitian)		$\mathbf{H}_0+\mathbf{H}_1+\mathbf{H}_2^{(2)}$

In this matrix RRHO energies and parallel Coriolis energies [cf. Eq. (2.2)] are along the main diagonal as, respectively, $\mathbf{H}_0$ and $\mathbf{H}_1$. For $\Delta K = -1$ the first two states form the resonant subspace in the partitioning method.[64] The third state, although coupled to the initial $|14^1;J,K\rangle$ by $\mathbf{H}_3^{(2)}$, forms the off-resonant subspace, being far removed in energy.

F. Coupling of the 14^1 state to the $3^1 16^1$ manifold

In the coupling of the 14^1 initial state to the $3^1 16^1$ manifold, the relevant coupling term, containing one rotational and three vibrational operators, is of order λ^2. Thereby, the twice-transformed Hamiltonian $\mathbf{H}^{(2)}$, which is diagonal to order λ^2 in the vibrational quantum numbers v_s, will fail to model an avoided crossing because $\mathbf{S}_2$ would contain small denominators of the form $\omega_{14} - \omega_3 - \omega_{16}$. Thereby, a modified transformation function $\mathbf{S}_2^*$ is applied to the untransformed Hamiltonian to obtain the coupling, $\mathbf{S}_2^*$ defined analogously to Eq. (2.19),

$$\mathbf{S}_2^* = i\frac{\mathbf{Q}_0^*}{\mathbf{a}}\mathbf{H}_2^{(1)}\mathbf{P}_0 + \text{h.c.}, \tag{2.28}$$

where $\mathbf{Q}_0^*$ is the projector $\Sigma_{k \neq k_{\text{res}}} |k\rangle\langle k|$, the sum over all zeroth-order states except the two quasidegenerate states of interest. The resulting 3×3 matrix is given by

$3^1 16^1$	$6^2 11^1$	14^1	$6^2 11^1$	$3^1 16^1$
$\lvert l_{16}^{+1};J,K-1\rangle$	$\lvert l_6^{-2};J,K-1\rangle$	$\lvert J,K\rangle$	$\lvert l_6^{+2};J,K+1\rangle$	$\lvert l_{16}^{-1};J,K+1\rangle$
$\mathbf{H}_0 + \mathbf{H}_2^{(2)}$	$\mathbf{H}_3^{(2)}$ quintic	$\mathbf{H}_2^{(2)}$	0*	$\mathbf{H}_2^{(2)}$ rot
	$\mathbf{H}_0 + \mathbf{H}_1 + \mathbf{H}_2^{(2)}$	$\mathbf{H}_3^{(2)}$	0	0*
		$\mathbf{H}_0 + \mathbf{H}_2^{(2)}$	$\mathbf{H}_3^{(2)}$	$\mathbf{H}_2^{(2)}$
			$\mathbf{H}_0 + \mathbf{H}_1 + \mathbf{H}_2^{(2)}$	$\mathbf{H}_3^{(2)}$ quintic
(Hermitian)				$\mathbf{H}_0 + \mathbf{H}_2^{(2)}$

This matrix employs $\mathbf{H}_2^{(2)}$ obtained with the modified $\mathbf{S}_2^*$ transformation function defined by Eq. (2.28), in order to avoid small denominators (arising from $1/\mathbf{a}$) of the form $\omega_{14} - \omega_3 - \omega_{16}$. Aside from this change, the only items in this matrix that have not been described in previous subsections are the off-diagonal terms $\mathbf{H}_3^{(2)}$ quintic and 0*. $\mathbf{H}_3^{(2)}$ quintic is a third-order anharmonic coupling of pairs of states in the $3^1 16^1$ and $6^2 11^1$ manifolds. There is also a parallel Coriolis term coupling the same states, but it is of order λ^4 and may be neglected. 0* is a high-order rotational l-doubling term, and is similarly neglected.

G. Coupling of the 14^1 state to the $6^2 11^1$ and $3^1 16^1$ manifolds

In order to treat several aspects of the fluorescence spectrum following excitation of states dominantly 14^1 in character,[8] for certain values of (J,K) (in particular $K = 15,17$) it is desirable to consider the simultaneous interaction of zeroth-order states from both the $6^2 11^1$ and $3^1 16^1$ manifolds, with 14^1 states. The resulting 5×5 matrix contains as basis states the $|14^1;J,K\rangle$ initial state, and the four final states included in the two 3×3 matrices above:

$\lvert l_{16}^{+1};J,K-1\rangle$	$\lvert 14^1;J,K\rangle$	$\lvert l_{16}^{-1};J,K+1\rangle$
$\mathbf{H}_0 + \mathbf{H}_2^{(2)}$	$\mathbf{H}_2^{(2)}$	$\mathbf{H}_2^{(2)}$ rot
	$\mathbf{H}_0 + \mathbf{H}_2^{(2)}$	$\mathbf{H}_2^{(2)}$
(Hermitian)		$\mathbf{H}_0 + \mathbf{H}_2^{(2)}$

In this matrix the vibrational label $3^1 16^1$ in the first and third columns is omitted. This matrix differs principally from the previous 3×3 matrix in that there is no parallel Coriolis energy along the main diagonal for the two dark states. The latter two states, differing in their K quantum numbers, are separated in zeroth order by their different rigid rotor energies contained in $\mathbf{H}_0$. The off-diagonal terms $\mathbf{H}_2^{(2)}$ couple 14^1 to the two $3^1 16^1$ states. $\mathbf{H}_2^{(2)}$ rot is a rotational l- doubling term that couples states via $\langle l_t;K|\mathbf{H}_2^{(2)}\text{ rot}|l_t \pm 2;K \mp 2\rangle$ and, for values of K of our interest, yields a coupling matrix element of magnitude 10^{-3} to 10^{-4} cm^{-1}, considerably smaller than the magnitude of $\mathbf{H}_2^{(2)}$.[67]

III. RESULTS FOR 14^1 S_1 STATE

A. Theoretical

A particular initial rovibronic state and a final state will be quasidegenerate provided that the (J,K) pair satisfies Eq. (3.3) given below. For these quasidegenerate pairs, the off-diagonal coupling can lead to significant deviations from line positions in the vicinity of the avoided crossings. In Fig. 4 of the article[5] of Riedle and Neusser, the avoided crossings involving the 14^1 state arrange themselves into two sets of resonance regions in the (J,K) rotational manifold; a region for coupling to $5^1 10^1 16^1$, ranging, for the best plots, from (35, 10) to (24, 9), and a region for $6^2 11^1$, ranging, for the best plots, from (35, 15) to (21, 17).[68] These avoided crossings are indicated in Tables I through IV, together with the final states to which the 14^1 state is coupled.[68]

For the light ($|14^1;J,K\rangle$) and dark rovibronic states to be nearly degenerate energies, as in Eq. (3.1), where $E_i^{(0)}$ is

TABLE I. Vibrational coupling constant for $\mathbf{H}_3^{(2)}$ interaction between the initially prepared 14^1 state and the final, dark states indicated.

K	Final state[a]	V_0,2×2 (10^{-4} cm^{-1})	V_0,5×5[c] (10^{-4} cm^{-1})	$\overline{V}_0$ (10^{-4} cm^{-1})	V_0, expt[b] (10^{-4} cm^{-1})
9	$5^1 10^1 16^1$	6.3	6.2	6.2	11.2
10	$5^1 10^1 16^1$	6.2	6.2	6.2	11.6
12	$5^1 10^1 16^1$	6.2	6.1	6.2	(9.8)
11	$6^2 11^1$	8.9	8.8	8.9	(8.1)
13	$6^2 11^1$	8.9	8.8	8.9	(9.7)
15	$6^2 11^1$	9.0	9.0	8.9	12.8
16	$6^2 11^1$	9.1	9.0	8.9	(17.1)
17	$6^2 11^1$	9.1	9.0	8.9	12.7

[a] $\Delta K = +1$ for $5^1 10^1 16^1$, -1 for $6^2 11^1$.
[b] Parentheses indicate less reliable values (see the text).
[c] 3×3 in the case of $6^2 11^1$.

defined by the first equality and $E_f^{(0)}$ by the last,

$$E_i^{(0)} = E_i^{\text{vib}} + E_i^{\text{rot}} + E_i^{\text{cor}} \approx E_f^{\text{vib}} + E_f^{\text{rot}} + E_f^{\text{cor}} = E_f^{(0)} \tag{3.1}$$

should be close for any such suitable final state, with $\Delta K = \pm 1$. The vibrational plus rotational energy is given by the RRHO approximation,[69] and the Coriolis energy in the $6^2 11^1$ final state is given in Eq. (2.2) by

$$E_f^{\text{cor}} = -(K \pm 1) B l_6 \zeta_{6a,6b}^{(z)}. \tag{3.2}$$

In contrast the final state $5^1 10^1 16^1$ has no first order Coriolis energy. Equations (3.1) and (3.2) yield for appropriate values of J and K, for the 14^1 and $6^2 11^1$ states,

$$E_f^{(0)} - E_i^{(0)} = \Delta B \left[J(J+1) - \frac{1}{2} K^2 \right] \mp B_f (1 \pm \sum_i l_i \zeta_i) K + (E_f^{\text{vib}} - E_i^{\text{vib}}) \approx 0, \quad (\Delta K = \pm 1), \tag{3.3}$$

where ΔB is the rotational constant of the final (dark) state (B_f) minus that of the initial (light) state. In the application of Eq. (3.3) to obtain a coupling element from the perturbation of the line position, for any given final state f, $E_f^{\text{vib}} - E_i^{\text{vib}}$ is constant when J and K are varied. The experimental plot is of differences of line positions vs J, or, in the present paper, vs $J(J+1)$, at fixed K. The constant $E_f^{\text{vib}} - E_i^{\text{vib}}$ does enter into the fitting, because of the square root, as seen later in Eqs. (3.4)–(3.6). The E_2' and E_1' appearing in Eq. (2.27) are the $E_f^{(0)}$ and $E_i^{(0)}$ of Eq. (3.3), but modified by the diagonal part of $\mathbf{H}_2^{(2)}$ and by the partitioning.

The avoided crossing plots given later are made at fixed K. As is seen from the functional form in Eq. (2.27), the difference in eigenvalues $E_f - E_i$ is given by

$$E_f - E_i = \pm \left[(E_f' - E_i')^2 + 4 |H_3^{(2)\prime}|^2 \right]^{1/2}. \tag{3.4}$$

The use of the form Eq. (3.3) for $E_f' - E_i'$ (omitting any functional modification caused by the $\mathbf{H}_3^{(2)}$ and partitioning terms) yields at fixed K, a functional form for $E_f' - E_i'$:

$$E_f' - E_i' = \Delta B J(J+1) - D, \tag{3.5}$$

where D is independent of J and is seen to be the value of $\Delta B J(J+1)$ at the "crossing point" of a plot of $E_f' - E_i'$ vs $J(J+1)$. $|H_3^{(2)\prime}|$ denotes the magnitude of the matrix ele-

TABLE II. Changes in rotational constant between the initial and final vibrational states (ΔB).[a]

K	Final state	ΔB,2×2 (10^{-4}cm^{-1})	ΔB,5×5[c] (10^{-4}cm^{-1})	$\Delta\overline{B}$ (10^{-4}cm^{-1})	ΔB, expt[b] (10^{-4}cm^{-1})
9	$5^1 10^1 16^1$	−3.0	−3.0	−3.0	−2.7
10	$5^1 10^1 16^1$	−3.0	−3.0	−3.0	−2.7
12	$5^1 10^1 16^1$	−3.0	−3.0	−3.0	(−2.7)
11	$6^2 11^1$	−4.9	−4.9	−5.0	(−4.1)
13	$6^2 11^1$	−4.9	−4.9	−5.0	(−4.1)
15	$6^2 11^1$	−4.9	−5.0	−5.0	−4.3
16	$6^2 11^1$	−5.0	−5.0	−5.0	(−4.6)
17	$6^2 11^1$	−5.0	−5.0	−5.0	−4.3

[a] $\Delta K = +1$ for $5^1 10^1 16^1$, -1 for $6^2 11^1$.
[b] Parentheses indicate less reliable values (see the text).
[c] 3×3 in the case of $6^2 11^1$.

TABLE III. Vibrational coupling constant for $H_2^{(1)}$ interaction between the initially prepared 14^1 state and the 3^116^1 state. The large disagreement between V_0 (expt) and V_0 (theor) argues against a quasidegeneracy of the 14^1 and 3^116^1 states.

K	Final state[a]	V_0,2×2 (10^{-4}cm^{-1})	V_0,3×3 (10^{-4}cm^{-1})	$\overline{V}_0$ (10^{-4}cm^{-1})	V_0, expt[b] (10^{-4}cm^{-1})
11	3^116^1	143.	142.	144.	(8.1)
13	3^116^1	143.	143.	144.	(9.7)
15	3^116^1	144.	143.	144.	12.8
16	3^116^1	144.	143.	144.	(17.1)
17	3^116^1	144.	143.	144.	12.7

[a] $\Delta K = -1$ in all transitions.
[b] Parentheses indicate less reliable values (see the text).

ment $\langle i|\mathbf{H}_3^{(2)\prime}|j\rangle$ for the relevant states, and is written in terms of the theoretically motivated expression

$$|\langle i|\mathbf{H}_3^{(2)\prime}|j\rangle| = V_0\,[J(J+1) - K(K\pm 1)]^{1/2}, \qquad (3.6)$$

even though it will not be exactly of this form, because of the partitioning contribution to $\langle i|\mathbf{H}_3^{(2)\prime}|f\rangle$. When the partitioning contribution to $\langle i|\mathbf{H}_3^{(2)\prime}|j\rangle$ is negligible, as we shall see it is to be in the present case, Eq. (3.6) becomes the correct functional form.

The principal theoretical contribution to $|\langle i|\mathbf{H}_3^{(2)\prime}|j\rangle|$ in Eqs. (3.4)–(3.6) is $|\langle i|\mathbf{H}_3^{(2)}|j\rangle|$ in each of these theoretical calculations; $|\langle i|\mathbf{H}_3^{(2)}|j\rangle|$ is a product of two terms, which can be written as

$$|\langle i|\mathbf{H}_3^{(2)}|j\rangle| = \overline{V}_0\,[J(J+1) - K(K\pm 1)]^{1/2}, \qquad (3.7)$$

where $\overline{V}_0$ in Eq. (3.7) is independent of J and K. The theoretical value of $\overline{V}_0$ is obtained as a sum, as given in Tables III and IV of Ref. 48, and is evaluated using the relevant molecular constants.[70] The latter include the harmonic frequencies, cubic and quartic force constants,[35] Coriolis coupling coefficients, inertial derivatives, and the Ω coefficients that appear in the expansion of the inverse inertia tensor in Eq. (2.7). Formulas for inertial derivatives and Ω-coefficients are available.[71] In addition to the anharmonic force constants given in Ref. 35, an incomplete listing, the additional constants in Appendix C were employed. Coriolis coupling coefficients were computed from the harmonic force field of Goodman *et al.*,[72] while existing formulas[71] were used to obtain inertial derivatives and Ω coefficients. Substitution of these constants into the sum noted above[48] yielded the set of theoretical $\overline{V}_0$ values listed in Tables I and III. The computed coupling constants are complex-valued quantities but only their magnitudes appear in the energy expression, and so only their magnitudes are reported here in Tables I and III.

The principal theoretical contribution to ΔB is $\Delta\overline{B}$, the difference in rotational constants of the relevant zeroth-order states in the absence of contributions from the partitioning. The theoretical $\Delta\overline{B}$ values are listed in Tables II and IV, together with the theoretical ΔB values as defined by Eqs. (3.4)–(3.6).

These coupling constants V_0 and ΔB were computed using the 5×5 (for $5^110^116^1$) and 3×3 (for 6^211^1 and 3^116^1) matrices given in Sec. II. The use of the 5×5 matrix containing both 6^211^1 and 3^116^1 states gave coupling constants for coupling of 14^1 to either one of these dark states within a few percent of the values obtained using the relevant 3×3 matrix containing that dark state. Thereby, we do not report separate coupling constants based upon this 5×5 matrix. The relevance of this 5×5 matrix is seen when the various peaks in the experimental fluorescence spectrum is interpreted.[8]

The difference in the two relevant eigenvalues of the 5×5 matrix for the coupling to the $5^110^116^1$ state and of the 3×3 matrices for the coupling to the 6^211^1 and 3^116^1 states are each fitted to Eqs. (3.4)–(3.6) to obtain theoretical V_0 and ΔB values, defined by these equations, and are listed in

TABLE IV. Changes in rotational constant between the initial state and the 3^116^1 final state (ΔB).[a]

K	Final state	ΔB,2×2 (10^{-4}cm^{-1})	ΔB,3×3 (10^{-4}cm^{-1})	$\Delta\overline{B}$ (10^{-4}cm^{-1})	ΔB, expt[b] (10^{-4}cm^{-1})
11	3^116^1	−6.6	−6.6	−6.5	(−4.1)
13	3^116^1	−6.6	−6.6	−6.5	(−4.1)
15	3^116^1	−6.6	−6.5	−6.5	−4.3
16	3^116^1	−6.5	−6.5	−6.5	(−4.6)
17	3^116^1	−6.5	−6.5	−6.5	−4.3

[a] $\Delta K = -1$ in all transitions.
[b] Parentheses indicate less reliable values (see the text).

Tables I through IV. The eigenvalues of the 2×2 matrix resulting from the partitioning (discussed below) are also fitted to Eqs. (3.4)–(3.6) and the resulting V_0 and ΔB values are also given in Tables I through IV.

B. Fit of Eqs. (3.4)–(3.6) to data and extraction of V_0,ΔB

We consider next the extraction of experimental values of V_0 and ΔB from the experimental data. The empirical least squares fit to the experimental avoided crossings in Fig. 4 of Riedle and Neusser is given in Figs. 1 and 2,[5] but plotted vs the present theoretically motivated $J(J+1)$.[73] These fits were made[74] using as unperturbed energies the rotational energies of Eq. (2.2), and as such do not include terms functionally of the form of quartic centrifugal distortion coefficients. The quality of the empirical fits is evident for $K=9$, 10, 15, and 17 (Fig. 1). This fit is less adequate for $K=11$, 12, 13, and 16 (Fig. 2), partly due to the smaller number of data points available for these values of K, and partly due to a possible overlap in some of the avoided crossings. Otherwise, the agreement of experimental curves with the empirical fits is quite good. The empirical fits of Eqs. (3.4)–(3.6) to the experimental data provide in Tables I through IV the experimental[74] values of V_0 and ΔB, parameters defined by the functional forms Eqs. (3.4) to (3.6).

IV. DISCUSSION

Due to the relatively low excess vibrational energy available in the 14^1 initial state ($1570\,\mathrm{cm}^{-1}$), the vibrational density of states is low, about 1 per cm^{-1}. As a result it was possible in the present case for the light state to couple to particular dark states (the coupling producing the avoided crossings being very small), rather than coupling to numerous dark states. Coupling to a large number of states would have caused a broadening and even a disappearance of some lines, rather than merely perturbation of some line positions.

For coupling to the $5^110^116^1$ manifold, for which there were four possible states $l_{10}=\pm1$, $l_{16}=\pm1$, only the ($l_{10}=-1$, $l_{16}=+1$) state is observed[75] to couple via $\mathbf{H}_3^{(2)}$ to the 14^1 state with the selection rule $\Delta K=+1$. (Had ΔK been -1, then the ($l_{10}=+1$, $l_{16}=-1$) state would have been coupled to the 14^1 state, and substantially the same calculated V_0 and ΔB would have been obtained.) The ($l_{10}=+1$, $l_{16}=-1$) and ($l_{10}=-1$, $l_{16}=+1$) states are mutually coupled via $\mathbf{H}_2^{(2)}$ as in the indicated matrix given earlier.

For the 6^211^1 final manifold, the observation[75] of $\Delta K=-1$ is consistent with a coupling of $l_6=-2$ via $\mathbf{H}_3^{(2)}$ to the initial state, according to the selection rule in Eq. (2.25). [There are possible states $l_6=\{+2,0,-2\}$, of which the $l_6=+2$ state couples via $\mathbf{H}_3^{(2)}$ to the initial state with $\Delta K=+1$, while the $l_6=0$ state does not couple (x,y)-Coriolis couple to the initial state.]

For the 3^116^1 final state, for which there were possible states $l_{16}=\{-1,+1\}$, $l_{16}=+1$ is coupled via $\mathbf{H}_2^{(1)}$ to the initial state with $\Delta K=-1$. (The $l_{16}=-1$ state is coupled via $\mathbf{H}_2^{(1)}$ to the initial state with $\Delta K=+1$.)

The coupling $|\langle i|\mathbf{H}_3^{(2)}|j\rangle|$ of the 14^1 and the $5^110^116^1$ final state had a $\overline{V}_0$ of $6.2\times10^{-4}\,\mathrm{cm}^{-1}$ and arose from some 77 symmetry-allowed terms in $|\langle i|\mathbf{H}_3^{(2)}|j\rangle|$ for these states (not including permutations of $\mathbf{p}$ and $\mathbf{q}$ operators). This number, although far less than the thousands of possible terms that might be nonzero prior to application of group theory, indicates the need for a computer to obtain even the elements of the 2×2 partitioned matrix for the calculation of $\overline{V}_0$. This $\overline{V}_0$ of $6.2\times10^{-4}\,\mathrm{cm}^{-1}$ due to the 77 terms includes $5.8\times10^{-4}\,\mathrm{cm}^{-1}$ from terms originating in products of untransformed operators $\mathbf{H}_{30}\mathbf{H}_{30}\mathbf{H}_{21}$. There were 70 independent such symmetry-allowed products. There was no contribution to $\overline{V}_0$ arising from the products $\mathbf{H}_{40}^{\mathrm{quartic}}\mathbf{H}_{21}$ (three terms) since in the absence of better data we have set the relevant quartic constants to zero.[76] The contribution of the products $\mathbf{H}_{30}\mathbf{H}_{31}$ (four terms) was $0.4\times10^{-4}\,\mathrm{cm}^{-1}$. The $\mathbf{H}_{41}$ gave no contribution in this case. Table V lists the cubic and quartic force constants entering into such products.

For coupling of the 14^1 state to the final state 6^211^1 a $\overline{V}_0$ of $8.9\times10^{-4}\,\mathrm{cm}^{-1}$ had contributions from 92 symmetry-allowed terms, not counting permutations of vibrational operators. This $\overline{V}_0$ of $8.9\times10^{-4}\,\mathrm{cm}^{-1}$ arose entirely from terms originating in products of untransformed operators $\mathbf{H}_{30}\mathbf{H}_{30}\mathbf{H}_{21}$, there being 86 independent such nonzero products, since there was no contribution to $\overline{V}_0$ arising from the products $\mathbf{H}_{40}^{\mathrm{quartic}}\mathbf{H}_{21}$ (six terms), owing to the zero values assumed for the relevant quartic constants.[76] Again, Table V lists the cubic and quartic force constants entering into such products.

For coupling of the 14^1 state to the final state 3^116^1 a $\overline{V}_0$ of $144\times10^{-4}\,\mathrm{cm}^{-1}$ had contributions from four symmetry-allowed terms, not counting permutations of vibrational operators. This $\overline{V}_0$ of $144\times10^{-4}\,\mathrm{cm}^{-1}$ arises solely from terms originating in products of untransformed operators $\mathbf{H}_{30}\mathbf{H}_{21}$, there being four independent such nonzero products. Far fewer nonzero products arise in this case because the single contact transformation using $\mathbf{S}_1$ introduces less terms than that arising from application of both $\mathbf{S}_1$ and $\mathbf{S}_2$. The relevant cubic force constants are listed in Table V.

The agreement of the theoretical and experimental values of V_0 in Table I is seen to be reasonable, considering the approximate nature of the present potential energy surface of S_1 benzene. It is seen from Table I that the theoretical value of $\overline{V}_0$ is very close to that of V_0. In the final column of that table are the experimental values of V_0 obtained from fitting the plots of the results of Neusser and co-workers to Eqs. (3.4)–(3.6).[7] The vibrational factors of V_0 of Table I, upon insertion into Eq. (3.4) together with typical values for J and K of, respectively, 30 and 10, gives a coupling of 2 to $3\times10^{-2}\,\mathrm{cm}^{-1}$. From Table II it is also seen that the theoretical value of $\Delta\overline{B}$ and the experimental values of ΔB differ only by some 15%. From Tables III and IV it is evident that, for the relevant values of (J,K), the 3^116^1 state is not a resonant contributor to the observed avoided crossings, the discrepancy between calculated and experimental V_0's now being a factor of about 10. Thereby, we infer, the 14^1 and 6^211^1 states should be nearly resonant, being the principal participants in the avoided crossing, with the 3^116^1 state perhaps

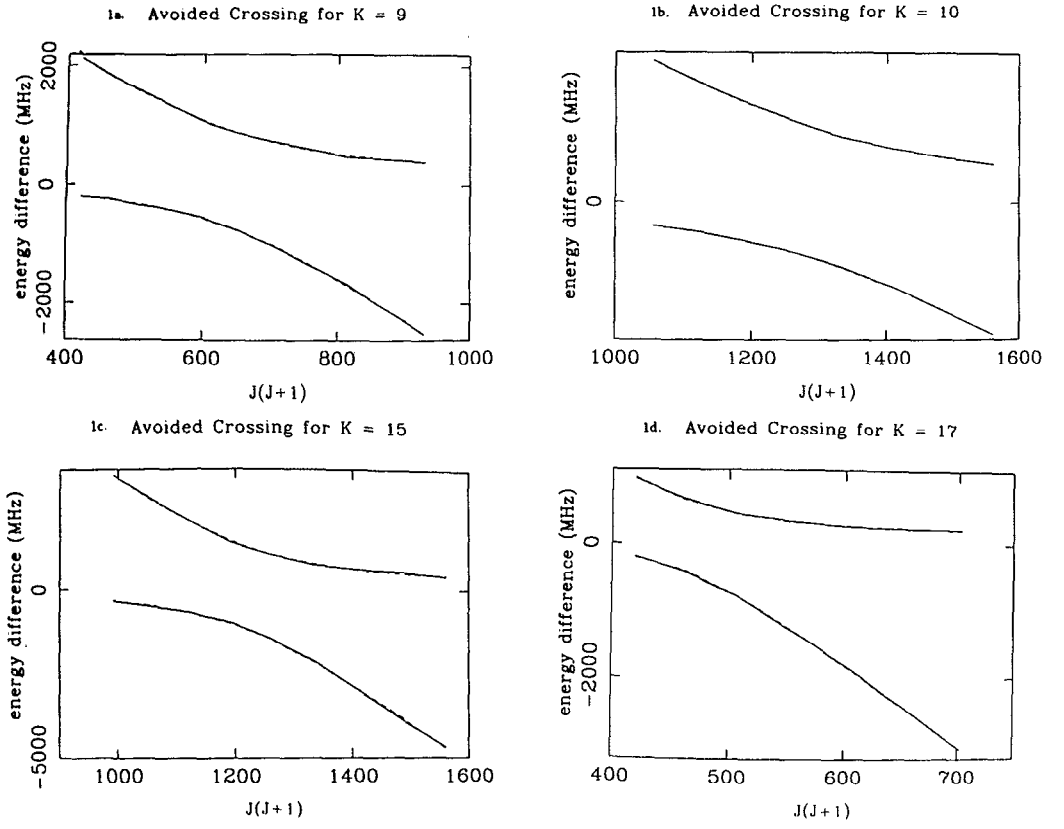

FIG. 1. Least squares fit to the avoided crossing for $K = 9$ with $5^1 10^1 16^1$ (a), $K = 10$ with $5^1 10^1 16^1$ (b), $K = 15$ with $6^2 11^1$ (c), $K = 17$ with $6^2 11^1$ (d). Solid line connects experimental points, dashed is the fit to the quadratic equation in Ref. 74.

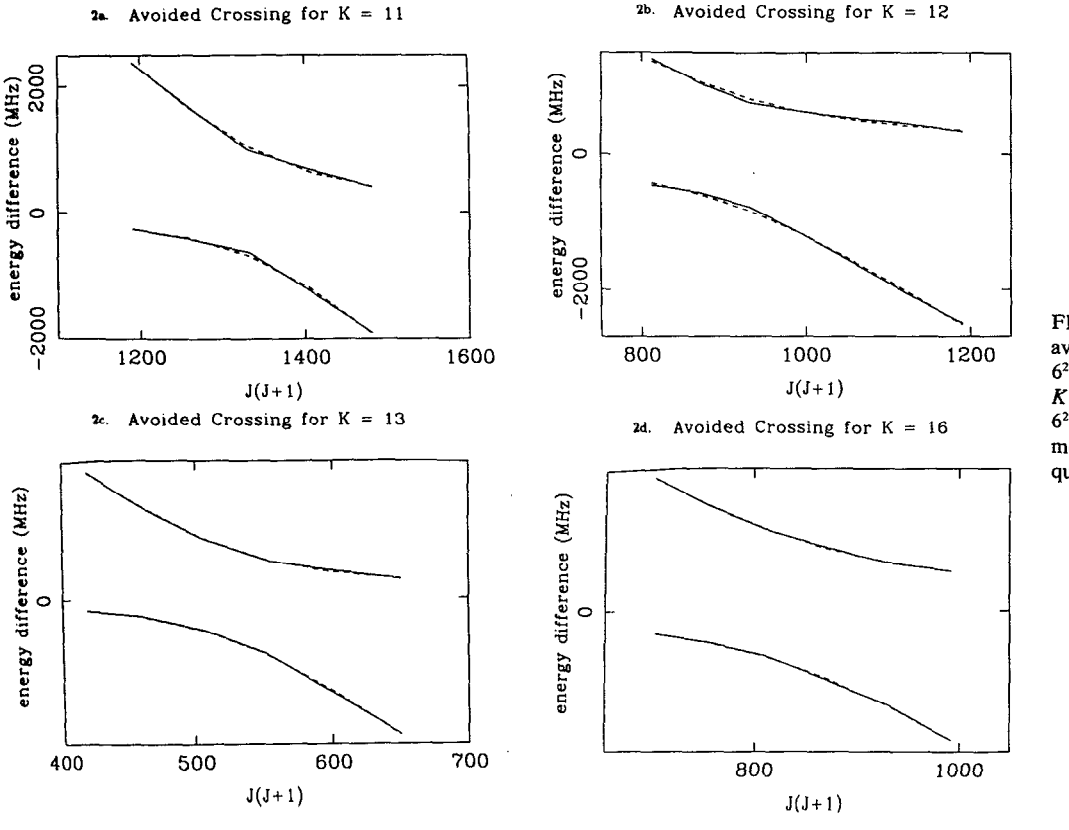

FIG. 2. Least squares fit to the avoided crossing for $K = 11$ with $6^2 11^1$ (a), $K = 12$ with $5^1 10^1 16^1$ (b), $K = 13$ with $6^2 11^1$ (c), $K = 16$ with $6^2 11^1$ (d). Solid line connects experimental points, dashed is the fit to the quadratic equation in Ref. 74.

TABLE V. Independent cubic force constants needed for coupling 14^1 to various states.[a]

Coupling to $5^1 10^1 16^1$ states
$i = 6$ to 9:
(14,18,*i*),(14,19,*i*),(14,20,*i*),(16,17,*i*),(11,16,*i*),(5,10,*i*)
$i = 18$ to 20:
(10,16,*i*),(10,11,*i*),(5,17,*i*),(10,17,*i*),(5,16,*i*)
$i = 12,13,15$:
(10,16,*i*)
Miscellaneous
(14,10,17),(14,5,11),(14,1,15),(14,2,15),(14,2,12),(14,2,13)
Quartic constants:
(4,10,14,16),(5,10,14,17),(5,10,15,16)
Coupling to $6^2 11^1$ states
$i = 6$ to 9:
(6,6,*i*)
$i = 6$ to 9 and $j = 16$ and 17:
(*i*,11,*j*)
$i = 6$ to 9 and $j = 18$ to 20:
(*i*,14,*j*)
Quartic constants:
(6,10,11,14)
(6,6,11,16),(6,6,11,17)
(6,6,14,18),(6,6,14,19),(6,6,14,20)
Coupling to $3^1 16^1$ states
(3,12,14),(3,16,16),(3,16,17),(10,14,16)

[a] Constants are k_{abc}, with *a,b,c* indicated in parentheses, or in the quartic case, k_{abcd}.

contributing via an off-resonance in the coupling of these states.

The present interpretation in terms of a perpendicular-type Coriolis coupling, involving (x,y) axes of rotation, is consistent with the experimental fact, noted by Neusser and co-workers,[7] that the splitting at the avoided crossing from different K's varies with J in a way characteristic of a perpendicular Coriolis coupling, namely it varies as $[J(J+1) - \frac{1}{2}K(K \pm 1)]^{1/2}$.

The coupling of the 14^1 to the $5^1 10^1 16^1$ state finds strong support, Schubert *et al.*[8] noted, in the appearance of the emission band $5_1^1 10_1^1 16_1^1 6_1^0$. (The mode Q_6, of e_{2g} symmetry, provides the vibronic activity needed in this otherwise forbidden electronic transition.) The coupling of the 14^1 state to the $6^2 11^1$ state is implicated by the appearance in emission of band systems $6_3^2 11_1^1 1_n^0$ and (but see below) $6_1^2 11_1^1 1_n^0$, the Q_6 mode again providing vibronic activity and Q_1, of a_{1g} symmetry, yielding the progressions. Based on a value given by Page *et al.*[39] a particular spectral emission peak could be attributed to $3_1^1 16_1^1 6_1^0 1_n^0$, corresponding to an involvement of the $3^1 16^1$ state: the possible Fermi resonance of $6^2 11^1$ and $3^1 16^1$, suggested in Ref. 8, and coupling to 14^1, are discussed later.

While the presence in emission of the $6_3^2 11_1^1 1_n^0$ system, and a band attributed to $3_1^1 16_1^1 6_1^0$ are consistent with the present analysis, the weakness of $6_1^2 11_1^1 1_n^0$ intensities, noted in Ref. 8, remains unexplained. It is relevant that the 6_3^2 and 6_1^2 intensities normally are in the ratio of two to one,[77] while in a separate study including excitation of the 6^2 band,[78] the intensity ratio for the emission bands $6_3^2 1_1^0$ and $6_1^2 1_1^0$ was about a factor of 3. Since the authors of this study found that 6^2 is in anharmonic resonance with the 11^2 state, one might conclude that mixed or combination states of Q_6 and Q_{11} might deviate in their Franck–Condon factors from the simple 6^2 state. Whether such an effect would yield a weak $6_1^2 11_1^1 1_1^0$ band intensity is presently not known. Other possible explanations are mentioned in Ref. 8, one being a possible displacement of the $6_1^2 11_1^1 1_1^0$ band from its anticipated position by some 70 cm^{-1}. Using the contact transformation formalism through S_2 for the coupling of $1_1 6_1 11_1$ and a nearby $8_1 11_1$ state (omitting the terms in S_2 which would yield small denominators but treating those terms via the diagonalization of the transformed Hamiltonian), we obtained a coupling matrix element of 28 cm^{-1}, which would be too small to yield a shift of 70 cm^{-1} in band position.[79]

V. CONCLUSION

Using a transformed Hamiltonian given by Nielsen and Amat,[46,48] obtained from contact transformations, the coupling between light and dark rovibronic states in S_1 benzene was evaluated. With it the perturbations in the line positions were calculated with terms involving a third-order perturbation of the vibration–rotation interaction. The coupling to the identified states led to a perpendicular Coriolis interaction between the nondegenerate initial state and the degenerate modes in the final dark states, modified by anharmonic coupling to other modes. While the evaluation of the coupling strength requires an accurate knowledge of cubic anharmonic force constants, the currently computed coupling strength is in reasonable agreement with observed line deviations, no adjustable parameters having been employed. The calculations also served to eliminate, by a factor of 10, a resonant coupling solely between the 14^1 state and the $3^1 16^1$ manifold.

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APPENDIX A: SOLUTION OF EQ. (2.8)

The solution of Eq. (2.8), as Eq. (2.11), can be found in Ref. 50 [cf. Eq. (7.6) and Eq. (A5) there], but a simple self-contained solution is given here for completeness.

Upon multiplying $\mathbf{H}_1^{(1)} - \mathbf{H}_1$ in Eq. (2.8) on the left and right by $\mathbf{P}_0 + \mathbf{Q}_0 = 1$ and using Eq. (2.10) it follows that

$$\mathbf{H}_1^{(1)} - \mathbf{H}_1 = -\mathbf{P}_0\mathbf{H}_1\mathbf{Q}_0 + \text{h.c.} \qquad \text{(A1)}$$

The $\mathbf{P}_0\mathbf{H}_1\mathbf{Q}_0$ in Eq. (A1) can be written as $\mathbf{P}_0\mathbf{H}_1(\mathbf{Q}_0/\mathbf{a})E_0 - \mathbf{P}_0\mathbf{H}_1(\mathbf{Q}_0/\mathbf{a})\mathbf{H}_0$, where $\mathbf{a} = E_0 - \mathbf{H}_0$.

Using $\mathbf{P}_0 E_0 = \mathbf{P}_0 \mathbf{H}_0 = \mathbf{H}_0 \mathbf{P}_0$ Eq. (A1) becomes

$$\mathbf{H}_1^{(1)} - \mathbf{H}_1 = \mathbf{P}_0 \mathbf{H}_1 (\mathbf{Q}_0/\mathbf{a}) \mathbf{H}_0 - \mathbf{H}_0 \mathbf{P}_0 \mathbf{H}_1 (\mathbf{Q}_0/\mathbf{a}) + \text{h.c.} \quad \text{(A2)}$$

The right-hand side of Eq. (A2) can thus be written as a commutator with $\mathbf{H}_0$:

$$\mathbf{H}_1^{(1)} - \mathbf{H}_1 = [\mathbf{P}_0 \mathbf{H}_1 (\mathbf{Q}_0/\mathbf{a}) - (\mathbf{Q}_0/\mathbf{a}) \mathbf{H}_1 \mathbf{P}_0, \mathbf{H}_0]. \quad \text{(A3)}$$

Comparison of Eq. (A3) with Eq. (2.8) shows that $\mathbf{S}_1$ and $\mathbf{P}_0 \mathbf{H}_1 (\mathbf{Q}_0/\mathbf{a}) - (\mathbf{Q}_0/\mathbf{a}) \mathbf{H}_1 \mathbf{P}_0$ differ at most by a quantity which commutes with $\mathbf{H}_0$. However, Eq. (2.8) shows that $\mathbf{S}_1$ can be determined only up to a quantity which commutes with $\mathbf{H}_0$. We set that quantity equal to zero, so that $\mathbf{S}_1$ vanishes when the perturbation vanishes. Thereby, Eq. (2.12) for $\mathbf{S}_1$ follows.

Equation (2.14) for $\mathbf{S}_2$ is the same as Eq. (2.8) for $\mathbf{S}_1$, apart from $\mathbf{H}_2^{(2)}$ and $\mathbf{H}_2^{(1)}$ replacing $\mathbf{H}_1^{(1)}$ and $\mathbf{H}_1$, respectively. Thereby, the solution for $\mathbf{S}_2$ is the same as Eq. (2.12) upon making these substitutions, so yielding Eq. (2.19).

APPENDIX B: SYMMETRY PROPERTIES OF Ω COEFFICIENTS, AN EXAMPLE

An example is given in this Appendix of the application of symmetry considerations to some of the terms which contribute to $\mathbf{H}_3^{(2)}$, namely, $\mathbf{H}_{41}$, $\mathbf{H}_{30}\mathbf{H}_{31}$, and $\mathbf{H}_{30}\mathbf{H}_{30}\mathbf{H}_{21}$.

The higher order Coriolis operator $\mathbf{H}_{31}$ results from a modification of $\mathbf{H}_{21}$ by motion along a normal coordinate Q_{a,σ_a} which distorts the molecule, thereby providing the additional inertial terms $\Sigma_{\alpha\beta} \Omega_{a,\sigma_a}^{(1)\alpha\beta} Q_{a,\sigma_a}$, $\alpha,\beta = x,y,z$. Both $\mathbf{H}_{31}$ and $\mathbf{H}_{12}$ contain $\Omega_{a,\sigma_a}^{(1)\alpha\beta} Q_{a,\sigma_a}$,[80] and we can readily learn about the properties of the latter by considering $\mathbf{H}_{12}$. We then apply the results to $\mathbf{H}_{31}$.

The two rotational operators $\mathbf{J}_\alpha$ and $\mathbf{J}_\beta$ in $\mathbf{H}_{12}$ appear only in the relevant forms $\mathbf{J}_\alpha \mathbf{J}_\beta + \mathbf{J}_\beta \mathbf{J}_\alpha$ when $\alpha \neq \beta$, and as $\mathbf{J}_x^2 + \mathbf{J}_y^2$, $\mathbf{J}_x^2 - \mathbf{J}_y^2$, or as $\mathbf{J}_z^2$. (The $\mathbf{J}_x^2 \pm \mathbf{J}_y^2$ arise according as $\partial \mu^{xx}/\partial Q_{a,\sigma_a} = \pm \partial \mu^{yy}/\partial Q_{a,\sigma_a}$ for the given Q_{a,σ_a}.) The irreducible representation for the product of $\mathbf{J}$'s is a_{1g} for the combinations in $\alpha\beta$ of $xx + yy$ and zz, e_{2g} for $xx - yy$ and xy, and e_{1g} for $xz(=zx)$ and $yz(=zy)$. The above linear combinations transform in the same fashion as components of the polarizability tensor.[81]

Since any term in the Hamiltonian must be invariant to all symmetry operations, a necessary condition for $\Omega_{a,\sigma_a}^{(1)\alpha\beta}$ in $\mathbf{H}_{12}$ to be nonzero is that $\Gamma(Q_{a,\sigma_a})$ be one of the above irreducible representations for some combination in $\alpha\beta$, for only such a Γ will contain an a_{1g} component in the representation of the triple product. Thereby, when $\alpha\beta = xx + yy$ or zz only a_{1g} modes have nonzero $\Omega_{a,\sigma_a}^{(1)\alpha\beta}$. For $\alpha\beta = xx - yy$ or xy it is nonzero only for e_{2g} modes. Since[82] $\Omega_{a,\sigma_a}^{(1)xz}$ and $\Omega_{a,\sigma_a}^{(1)yz}$ vanish for all modes in benzene, there are no terms in $\mathbf{H}_{12}$ for the combinations xz and yz. Equating like terms in expansions of the inertia tensor in terms of Cartesian components and in terms of the pairs $\alpha\beta$ used here, $\Omega_{a,\sigma_a}^{(1)xx \pm yy} = \Omega_{a,\sigma_a}^{(1)xx} \pm \Omega_{a,\sigma_a}^{(1)yy}$. In the calculations we have $\frac{1}{2}\Omega_a^{(1)xx+yy} = \Omega_a^{(1)xx} = \Omega_a^{(1)yy} = \frac{1}{2}\Omega_a^{(1)zz}$ for the a_{1g} case,[71] and $\frac{1}{2}\Omega_{a,1}^{(1)xx-yy} = \Omega_{a,1}^{(1)xx} = -\Omega_{a,1}^{(1)yy}$ and $\Omega_{a,2}^{(1)xy} = \Omega_{a,2}^{(1)yx}$ in the e_{2g} case.[71] In the W (Wilson)[32] system of numbering vibrational modes for benzene, Q_1 and Q_2 are each of the irreducible representation a_{1g}, and Q_6, Q_7, Q_8 and Q_9 the irreducible representation e_{2g}, so determining which terms in Q_{a,σ_a} contribute to $\Sigma_{\alpha\beta} \Omega_{a,\sigma_a}^{(1)\alpha\beta} Q_{a,\sigma_a}$ in $\mathbf{H}_{31}$ for the above $\alpha\beta$. All six of these modes are in-plane.

Of the three modes Q_{a,σ_a}, Q_{b,σ_b}, Q_{c,σ_c} contained in $\mathbf{H}_{31}$, nonzero terms occur when three of these Q's are in-plane (z coupling) or when two of the three modes are in-plane (x,y coupling), as seen by the following arguments. We consider the case where Q_{b,σ_b} and Q_{c,σ_c} are coupled by a Coriolis term, $\mathbf{J}_\alpha \mathbf{p}_\beta$ in Eq. (2.3), and mode Q_{a,σ_a} is the distortion coordinate. We first note that $\mathbf{J}_z \mathbf{p}_x$, $\mathbf{J}_x \mathbf{p}_z$, $\mathbf{J}_z \mathbf{p}_y$, and $\mathbf{J}_y \mathbf{p}_z$ are absent since, as noted above, all $\Omega_{a,\sigma_a}^{(1)xz}$ and $\Omega_{a,\sigma_a}^{(1)yz}$ vanish. For parallel (z) coupling, i.e., for $\mathbf{J}_z \mathbf{p}_z$, mode Q_{a,σ_a} must be a_{1g}, since as noted above only a_{1g} modes have nonzero $\Omega_{a,\sigma_a}^{(1)zz}$. Since all a_{1g} modes are in-plane it follows that this mode is also. The modes Q_{b,σ_b} and Q_{c,σ_c} coupled via the z-Coriolis term $\mathbf{J}_z \mathbf{p}_z$ must clearly also both be in-plane, to yield a z component of vibrational angular momentum. Thus all three modes are in-plane in this z-Coriolis term. For a perpendicular (x,y) coupling ($\mathbf{J}_x \mathbf{p}_x$, $\mathbf{J}_y \mathbf{p}_y$, $\mathbf{J}_x \mathbf{p}_y$ or $\mathbf{J}_y \mathbf{p}_x$) there is one in-plane and one out-of-plane mode, to yield an $x(y)$ component ($\mathbf{p}_x$ or $\mathbf{p}_y$) of vibrational angular momentum. Since all nonzero $\Omega_{a,\sigma_a}^{(1)\alpha\beta}$ arise from in-plane modes of a_{1g} or e_{2g} symmetry mode Q_{a,σ_a} is in-plane. Thus in the perpendicular coupling case, two of the three modes are in-plane and the third is out of plane.

The Coriolis operator $\mathbf{H}_{41}$ results from the modification of $\mathbf{H}_{21}$ by distortion along two coordinates Q_{a,σ_a} and Q_{b,σ_b}, thereby providing the inertial terms $\Sigma_{\alpha\beta} \Omega_{Q_{a,\sigma_a},Q_{b,\sigma_b}}^{(2)\alpha\beta} Q_{a,\sigma_a} Q_{b,\sigma_b}$. This term can be examined via $\mathbf{H}_{22}$, which also contains $\Omega_{Q_{a,\sigma_a},Q_{b,\sigma_b}}^{(2)\alpha\beta} Q_{a,\sigma_a} Q_{b,\sigma_b}$ terms.[80] We require that each term in $\mathbf{H}_{22}$ be a_{1g}, and hence that

$$\Gamma_{a_{1g}} \in \Gamma(Q_{a,\sigma_a}) \otimes \Gamma(Q_{b,\sigma_b}) \otimes \Gamma(\mathbf{J}_\alpha, \mathbf{J}_\beta), \quad \text{(B1)}$$

where $\Gamma(\mathbf{J}_\alpha, \mathbf{J}_\beta)$ is one of the representations for the $\mathbf{J}_\alpha \mathbf{J}_\beta$ terms mentioned earlier. Comparison with arguments given for $\mathbf{H}_{12}$ (and hence for $\mathbf{H}_{31}$) shows that, just as in that case $\Gamma(Q_{a,\sigma_a})$ must be a_{1g} or e_{2g}, so here $\Gamma(Q_{a,\sigma_a}) \otimes \Gamma(Q_{b,\sigma_b})$ must contain a_{1g} or e_{2g}, in order that Eq. (B1) be fulfilled. The number of symmetry-allowed possibilities which satisfy this condition are many and may be found from a character table.[81] In terms of the usual combinations in $\alpha\beta = xx, yy$, etc., $\cdots$ one has[71]

$$\Omega_{Q_{a,\sigma_a},Q_{b,\sigma_b}}^{(2)\alpha\beta} = \frac{3}{8} \sum_\gamma (I_{\gamma\gamma}^e)^{-1} (\Omega_{a,\sigma_a}^{(1)\alpha\gamma} \Omega_{b,\sigma_b}^{(1)\gamma\beta} + \Omega_{b,\sigma_b}^{(1)\alpha\gamma} \Omega_{a,\sigma_a}^{(1)\gamma\beta}), \quad (\gamma = x,y,z). \quad \text{(B2)}$$

This equation can be used to obtain $\Omega^{(2)}$'s for $\alpha\beta$ equal to various pairs of x, y, and z. The latter $\Omega^{(2)}$'s can then be used to obtain the group-theoretically motivated combinations $\Omega_{Q_{a,\sigma_a},Q_{b,\sigma_b}}^{(2)xx+yy}$ and $\Omega_{Q_{a,\sigma_a},Q_{b,\sigma_b}}^{(2)xx-yy}$. In all cases the resulting formulas, just as in Eq. (B2), indicate that the nonzero $\Omega_{Q_{a,\sigma_a}}^{(1)\alpha\beta}$ deter-

mine the nonzero $\Omega^{(2)\alpha\beta}_{Q_{a,\sigma_a},Q_{b,\sigma_b}}$.[83] Thereby, $\Gamma(Q_{a,\sigma_a})$ and $\Gamma(Q_{b,\sigma_b})$ must *individually* be a_{1g} or e_{2g}, since from Eq. (B2) both $\Omega^{(1)\alpha\gamma}_{Q_{a,\sigma_a}}$ and $\Omega^{(1)\gamma\beta}_{Q_{b,\sigma_b}}$ must be nonzero for some α, β, γ, and the $\Omega^{(1)}$'s are nonzero only for a_{1g} and e_{2g} modes. The results given earlier for the $\Omega^{(1)}$'s can thus be adapted to $\Omega^{(2)\alpha\beta}_{Q_{a,\sigma_a},Q_{b,\sigma_b}}$.

When in $\Omega^{(2)\alpha\beta}_{Q_{a,\sigma_a},Q_{b,\sigma_b}}$ $\alpha\beta = xx + yy$ and zz one finds that $\Gamma(Q_{a,\sigma_a}) = \Gamma(Q_{b,\sigma_b}) = \Gamma_{a_{1g}}$ and $\Gamma(Q_{a,\sigma_a}) = \Gamma(Q_{b,\sigma_b}) = \Gamma_{e_{2g}}$. When $\alpha\beta = xx - yy$ and xy $\Gamma(Q_{a,\sigma_a})$ and $\Gamma(Q_{b,\sigma_b})$ are a_{1g} and e_{2g}, respectively. When $\alpha\beta = xz$ and yz Eq. (B2) applies unaltered by transformation to our linear group-theoretic motivated combinations and the $\Omega^{(2)\alpha\beta}_{Q_{a,\sigma_a},Q_{b,\sigma_b}}$ vanish, noting Eq. (B2) and that all $\Omega^{(1)xz}_{Q_{a,\sigma_a}}$ and $\Omega^{(1)yz}_{Q_{a,\sigma_a}}$ are zero. For calculation of coefficients in $\mathbf{H}_{41}$ we employ the relations given earlier for $\mathbf{H}_{12}$ and $\mathbf{H}_{31}$, replacing $\Omega^{(1)}$ by $\Omega^{(2)}$.

Restrictions for the four vibrational modes which arise in $\mathbf{H}_{41}$, Q_{a,σ_a}, Q_{b,σ_b}, Q_{c,σ_c}, Q_{d,σ_d} analogous to those for $\mathbf{H}_{31}$. We consider the case where Q_{c,σ_c} and Q_{d,σ_d} couple via a Coriolis term and where Q_{a,σ_a} and Q_{b,σ_b} are the distortion coordinates. The latter two coordinates must both be in-plane, since they must individually transform as a_{1g} or e_{2g}, in order to have some nonzero $\Omega^{(2)\alpha\beta}_{Q_{a,\sigma_a},Q_{b,\sigma_b}}$. For perpendicular Coriolis coupling one member of Q_{c,σ_c} and Q_{d,σ_d} must be in-plane and one out-of-plane. Therefore, in this case three of the four modes are in-plane. Since for parallel coupling both modes coupled via an $\mathbf{H}_{21}$ Coriolis term are in-plane, now, therefore, all four modes in $\mathbf{H}_{41}$ are in-plane. In addition, for parallel (z) coupling, modes Q_a and Q_b must have the irreducible representations a_{1g}, recalling that $\Omega^{(2)zz}_{Q_{a,\sigma_a},Q_{b,\sigma_b}}$ is nonzero only for $\Gamma(Q_{a,\sigma_a}) = \Gamma(Q_{b,\sigma_b}) = a_{1g}$.

The following example illustrates the application of elementary group theory to the term $\mathbf{H}_{30}\mathbf{H}_{30}\mathbf{H}_{21}$, which contributes to $\mathbf{H}_3^{(2)}$ and to the determination of which products of the operators give a nonzero contribution.

The sum $\Sigma_b \Sigma_c C_{bc} k_{abc} k_{cde} \zeta^{\alpha}_{b,f} \mathbf{q}_a \mathbf{q}_d \mathbf{q}_e \mathbf{p}_f \mathbf{J}_\alpha$ given in Sec. II contributes to $\mathbf{H}_{30}\mathbf{H}_{30}\mathbf{H}_{21}$, and it is desired to find which values of b and c give a nonzero result for the coefficients. It is first noted that a, d, e, f are fixed as permutations of 5, 10, 14, 16, in the case of coupling of the 14^1 and the $5^1 10^1 16^1$ states. The allowed values of these four indices a, d, e, f are considered systematically. The term $f = 5$ is considered first as an illustration. Similar reasoning would follow for the remaining three choices of f.

For perpendicular coupling $\alpha = x,y$ and it is required for $\zeta^{\alpha}_{b,f}$ to be nonzero that $\Gamma(Q_b) \otimes \Gamma(Q_f)$ contain the irreducible representation e_{1g}.[81] Noting that $\Gamma(Q_5) = b_{2g}$ it is found that $\Gamma(Q_b) = e_{2g}$. Thereby, it follows that b is restricted to being 6,7,8,9 for a nonzero $\zeta^{\alpha}_{b,f}$. Considering k_{abc} next, there are three possible values of a, namely, 10, 14, and 16. Choosing $a = 14$ (similar reasoning would follow for the remaining two choices) then for $\Gamma(Q_a) \otimes \Gamma(Q_b) \otimes \Gamma(Q_c)$ to have an a_{1g} component,[84] noting that $\Gamma(Q_a) = \Gamma(Q_{14}) = b_{2u}$ and, it was seen, $\Gamma(Q_b) = e_{2g}$, it follows[81] that $\Gamma(Q_c) = e_{1u}$. Thereby, $\tau = 18,19,20$. For the given $a = 14$ and $f = 5$ we have d and e being 10 and 16. Choosing $e = 16$ with $\Gamma(Q_{16}) = e_{2u}$ and $\Gamma(Q_{10}) = e_{1g}$, then in k_{cde} the irreducible representation for the direct product $\Gamma(Q_c) \otimes \Gamma(Q_d) \otimes \Gamma(Q_e) = e_{1u} \otimes e_{1g} \otimes e_{2u}$ is $a_{1g} + a_{2g} + 3e_{2g}$, which contains an a_{1g} component, ensuring that k_{cde} is not zero by symmetry. The four values of $b(6,7,8,9)$, together with the three values of $c(18,19,20)$, indicates 12 independent, nonzero products $k_{abc}k_{cde}\zeta^{\alpha}_{b,f}$ from this source.

APPENDIX C: SOME RELEVANT FORCE AND OTHER COUPLING CONSTANTS

The cubic force constants used are taken from an *ab initio* force field for ground state benzene.[35] We have obtained from it the cubic force constants that involve only totally symmetric (a_{1g}) linear combinations of three vibrational operators, of which there are 237 independent values.[85] Out-of- plane cubic constants (involving Wilson's symmetry coordinates[32] γ and/or δ) were the most relevant.

A Morse oscillator model of stretching valence coordinates provided estimates of the diagonal (k_{aaaa}) and semi-diagonal (k_{aabb}) quartic constants, obtained from Ref. 86. For the remaining, quartic constants that are not zero by symmetry we have assumed a value of zero, since there is no data available for these constants.

Coriolis coupling constants were computed from the L matrix[29] obtained using the quadratic force field solution of Ref. 72. The ground electronic state values obtained from a normal mode analysis were assumed for calculating the present set of Coriolis coefficients $\zeta^{(\alpha)}_{k,l}$.

Inertial derivatives and higher order coefficients of the inverse inertia tensor were computed using the values $r_{CH} = 1.084$ Å and $r_{CC} = 1.397$ Å for the excited state carbon–hydrogen and carbon–carbon equilibrium bond lengths, respectively.

Evaluation of $\mathbf{H}_3^{(2)}$, needed for the leading terms (order λ^3) for coupling of 14^1 to the $5^1 10^1 16^1$ and to the $6^2 11^1$ states, depends upon knowledge of[48] the basic molecular parameters such as Coriolis coupling constants, cubic and quartic force constants, and inertial derivatives, i.e., derivatives of elements of the inertia tensor with respect to normal coordinates, $\partial I_{\alpha\beta}/\partial Q_k$, $\alpha,\beta = x,y,z$, and for the k th normal coordinate. Evaluation of $\mathbf{H}_2^{(1)}$ for the leading terms for coupling of the 14^1 to the $3^1 16^1$ state (order λ^2) requires these also, apart from the quartic force constants and the second derivatives of the inertia tensor. Considering these various parameters in turn, accurate data on Coriolis coupling parameters ζ^{α}_{kl} are obtained from geometrical considerations in conjunction with the harmonic potential. Thus the terms in $\mathbf{H}_3^{(2)}$ and $\mathbf{H}_2^{(1)}$ containing $\mathbf{H}_{21}$ (multiplied by other terms due to the transformation), posed no difficulty in calculation of quantitative higher order vibration–rotation coupling coefficients. Rather, it was the terms having their origin in operators such as $\mathbf{H}_{30}$, which involved cubic force constant data, which could reduce the accuracy of such a calculation. In the current absence of an excited state S_1 cubic force field it was expedient to use the ground state (S_0) values for the cubic and the few quartic anharmonic constants that appeared. There is a clear need, however, for cubic and quartic constants for the S_1 state of benzene.

In the evaluation of $\mathbf{H}_3^{(2)}$ rotational matrix elements are required, and because the spherical tensor operators $\mathbf{J}_\pm \equiv \mathbf{J}_x \pm i\mathbf{J}_y$ have simple matrix elements for rotational eigenfunctions, it is convenient to use them, with matrix elements[29]

$$\langle J,K|\mathbf{J}_\pm|J,K\pm1\rangle = \hbar[J(J+1)-K(K\pm1)]^{1/2}. \tag{C1}$$

The products of angular momentum operators $\mathbf{p}_x\mathbf{J}_x$ and $\mathbf{p}_y\mathbf{J}_y$ are expressed in terms of the products $\mathbf{p}_+\mathbf{J}_-$ and $\mathbf{p}_-\mathbf{J}_+$, where $\mathbf{p}_\pm = \mathbf{p}_x \pm i\mathbf{p}_y$, with well-known matrix elements for coupling involving two- dimensional isotropic oscillators.[29] The operators in Eqs. (2.3) and (2.4) are transformed into these operators in the calculation of coupling constants.

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[55] $\mathbf{S}^{\mathrm{vib}}_{1;p}$ contains only vibrational operators and $\mathbf{H}_{02}$ contains only rotational operators. Hence, $\mathbf{S}^{\mathrm{vib}}_{1;p}$ commutes with $\mathbf{H}_{02}$. Similarly $\mathbf{S}^{\mathrm{rot}}_{1;p}$ commutes with $\mathbf{H}_{20}$ since $\mathbf{S}^{\mathrm{rot}}_{1;p}$ contains only rotational operators and $\mathbf{H}_{20}$ contains only vibrational operators.
[56] Rotational operators in the Nielsen **S** functions may be treated as constants for the present purpose of comparing the two forms of the **S** functions.
[57] Whereas the $\mathbf{S}_{1;p}$ function necessitated by the term in $\mathbf{H}_1$ due to cubic anharmonicity has the simple form [cf. Eq. (2.12)] of a cubic force constant divided by an energy difference, the corresponding $\mathbf{S}_{1;p}$ function in the Nielsen formulation contains four terms, each a different polynomial in three vibrational operators. See Ref. 47.
[58] There are terms with 1 **p** and 3 **q** operators and terms with 1 **q** and 3 **p** operators. When four different vibrational modes are coupled the order of vibrational operators is immaterial, as in the coupling of 14^1 to $5^1 10^1 16^1$. When at least two of the operators are from the same mode (as in $\mathbf{q}_6$ and $\mathbf{p}_6$ in the case of coupling of 14^1 to $6^2 11^1$), the order becomes important due to commutation rules. The actual expressions used (Ref. 46) are Hermitian.
[59] For the $6^2 11^1$ final state the product operators which contribute have a common mode index for two of the four vibrational operators. Thus instead of $C_{bc}k_{abc}k_{cde}\zeta^a_{b,d}\mathbf{q}_a\mathbf{q}_d\mathbf{q}_e\mathbf{p}_f\mathbf{J}_\alpha$ one has $C_{bc}k_{abc}k_{cda}\zeta^a_{b,d}\mathbf{q}_a\mathbf{q}_d\mathbf{q}_d\mathbf{p}_f\mathbf{J}_\alpha$.
[60] The twice-transformed Hamiltonian $\mathbf{H}^{(2)}$, in a matrix representation of

RRHO basis states, will not be diagonal to order λ^2 with respect to l quantum numbers in the case of doubly degenerate vibrations. It will also not be diagonal with respect to rotational quantum number K. In their standard formulation Nielsen and co-workers did not include in $\mathbf{S}_2$ the terms $\mathbf{S}_{2;p}$ which correspond to terms in the Hamiltonian $\mathbf{H}_{2;p}^{(1)}$ that have matrix elements diagonal in the v_i but off-diagonal in the l_i, in the representation of RRHO basis states. A similar statement may be made for the quantum number K. See also Ref. 53.

[61] Reference 48, p. 87.

[62] Using ΔD_J of 10^{-9} cm^{-1} the typical contribution of quartic centrifugal distortion terms to energy differences between initial and final states is 10^{-4} cm^{-1}.

[63] Reference 29, p. 171.

[64] The main effect of switching the sign of ΔK is to change the sign within the rotational factor $[J(J+1) - K(K \pm 1)]^{1/2}$. For $K \ll J$ this step alters the coupling matrix element by a few percent. The sign of ΔK is chosen to agree with experiment (cf. Ref. 75).

[65] P. Lowdin, in *Perturbation Theory and its Applications in Quantum Mechanics*, edited by C. H. Wilcox (Wiley, New York, 1966).

[66] I. Levine, *Quantum Chemistry* (Allyn and Bacon, Boston, 1974).

[67] M. L. Grenier-Besson, J. Phys. Radium, **21**, 555 (1960).

[68] Since the computed coupling to $3^1 16^1$ is an order of magnitude larger than the observed coupling reported for these values of (J,K), we use the $6^2 11^1$ state in the discussion.

[69] E_{vib} also includes in the diagonal matrix elements of $\lambda^2 \mathbf{H}_2^{(2)}$ (a) terms that are independent of rotational quantum numbers and (b) (J,K)- dependent terms (Ref. 62) that are small enough to neglect in assignment of unperturbed lines.

[70] Reference 48, Chaps. II and III.

[71] Reference 48, Chap. I provides formula whereby $\Omega_{Q_{a,\sigma_a}}^{(1)\alpha\beta}$ and $\Omega_{Q_{a,\sigma_a}Q_{b,\sigma_b}}^{(2)\alpha\beta}$ may be calculated for $\alpha,\beta = x,y,z$. The numerical results yield the equalities indicated.

[72] A. G. Ozkabak and L. Goodman, J. Chem. Phys. **87**, 2564 (1987).

[73] The data in this figure taken from Ref. 7 were digitized and replotted as in Figs. 1 and 2. The resulting data are very close to the original ones. [H. J. Neusser (private communication)].

[74] Denoting the square of the difference in energies of pairs of states near an avoided crossing (with the same values of J_i and K) by y_i, in the present approximation one has $y_i = (\alpha x_i + \beta)^2 - \beta K(K-1)x_i + \gamma$, where $x_i = J_i(J_i+1)$, $\alpha = \Delta B$, $\beta = 4V_0^2$, and γ is dependent on K alone and hence is constant for a plot at fixed K. The least squares fit of this quadratic equation in $J_i(J_i+1)$ for α and β yields the difference in slopes ΔB, and V_0, the vibrational factor in the coupling matrix element.

[75] H. J. Neusser (private communication).

[76] The nonzero diagonal (k_{aaaa}) and semidiagonal (k_{aabb}) quartic force constants did not enter in the symmetry-allowed products.

[77] C. S. Parmenter, K. Y. Tang, and W. R. Ware, Chem. Phys. **17**, 359 (1976).

[78] T. A. Stephenson, P. T. Radloff, and S. A. Rice (private communication).

[79] A shift in band position of 70 cm^{-1} requires a coupling matrix element with at least this magnitude. A (J,K) dependence of this matrix element, such as in higher-order Coriolis coupling, would yield a smaller magnitude, and so only the purely vibrational contribution to such a possible coupling was calculated to see if it could account for a shift of 70 cm^{-1}.

[80] Reference 48, p. 10.

[81] Reference 32, App. X, p. 328.

[82] Terms in $\mathbf{J}_x\mathbf{J}_z$ or $\mathbf{J}_y\mathbf{J}_z$ arise [cf. Eq. (2.2)] from nonzero μ_{xz} or μ_{yz}, elements of the inverse inertia tensor μ. Since no single vibrational mode in benzene simultaneously distorts along the x (or y) and z axes, I_{xz} and I_{yz} vanish upon arbitrary distortion. Under such conditions μ_{xz} and μ_{yz} vanish (cf. Ref. 48, p. 6). One may verify either by inspection of the normal mode eigenvectors or by calculation, that for benzene only a_{1g} and e_{2g} modes have nonzero inertial derivatives and hence nonzero $\Omega_{a,\sigma_a}^{(1)\alpha\beta}$ for some pairs of $\alpha\beta$.

[83] Reference 48, p. 9.

[84] For the cubic constant k_{abc} to be nonzero the direct product of the irreducible representations of modes Q_a, Q_b, and Q_c must contain a totally symmetric (a_{1g}) component (cf. Ref. 32, Chap. VIII.).

[85] Y.-f. Zhang, S. J. Klippenstein, and R. A. Marcus, J. Chem. Phys. **94**, 7319 (1991); Y.-f. Zhang and R. A. Marcus (submitted for publication).